IRON AND STEEL
DIVISION

1938

TRANSACTIONS

OF THE

AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS

(INCORPORATED)

Volume 131

IRON AND STEEL DIVISION

1938

$\mathcal{N}otice$

This volume is the eleventh of a series containing papers and discussions presented before the Iron and Steel Division of the American Institute of Mining and Metallurgical Engineers since its organization in 1928; one volume each year, as follows:

1928, Iron and Steel Technology in 1928 (later listed as Volume 80 of the TRANSACTIONS); 1929 (vol. 84), 1930 (vol. 90), 1931 (vol. 95), 1932 (vol. 100), 1933, 1934, 1935, 1936, 1937, and 1938, TRANSACTIONS of the American Institute of Mining and Metallurgical Engineers, Iron and Steel Division.

This volume contains papers and discussions presented at the meetings at Atlantic City, Oct. 18–21, 1937; New York, Feb. 14–17, 1938, and Buffalo, April 20–22, 1938.

Papers on iron and steel subjects published by the Institute prior to 1928 are to be found in many volumes of the TRANSACTIONS of the Institute; in Vols. 37 to 45, inclusive; 47, 50 and 51, 53, 56, 58, 62, 67 to 71, inclusive; 73 and 75. Vol. 67 was devoted exclusively to iron and steel.

Iron and steel papers published in the TRANSACTIONS may be found by consulting the general indexes to Vols. 1 to 35 (1871–1904), Vols. 36 to 55 (1905–1916), Vols. 56 to 72 (1917–1925), and Vols. 73 to 117 (1926–1935), and the indexes in succeeding Year Books.

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FOREWORD

The present volume has something of interest to each of our members. Eight papers on blast-furnace problems, two on ingots, the very interesting paper on Professor Read's ancient Chinese castings, and one on the use of statistics in quality control; with nine good papers on general metallurgy and the excellent Howe Memorial Lecture make a well rounded book.

It is expected that the work of the newly organized Program Committee, under the chairmanship of Mr. R. C. Good, will tend to give succeeding volumes more of coherence and continuity, but it would be unfortunate if the scope of these volumes were narrowed too much.

A new feature is the inclusion of the index of the current Institute of Metals Division volume (Vol. 128). This is to be a feature of both volumes in the future and is expected to be a real convenience to the membership of the two divisions.

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JAMES T. MACKENZIE, *Chairman,*
Iron and Steel Division.

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BIRMINGHAM, ALA.
  August 15, 1938

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BYLAWS OF THE IRON AND STEEL DIVISION

(As approved by the Board of Directors, September 16, 1937)

ARTICLE I

NAME AND OBJECTS

SEC. 1. This Division shall be known as the Iron and Steel Division of the American Institute of Mining and Metallurgical Engineers.

SEC. 2. The objects shall be to furnish a medium of cooperation between those interested in the metallurgy and industry of iron and steel manufacture and use; to represent the A.I.M.E. in so far as ferrous metallurgy is concerned, within the rights given by A.I.M.E. Bylaw XVII, Section 3, and not inconsistent with the Constitution and Bylaws of the A.I.M.E.; to hold meetings for social intercourse and the discussion of ferrous metallurgy; to stimulate the writing, presentation and discussion of papers of high quality on ferrous metallurgy; to reject or accept such papers for presentation before meetings of the Division.

ARTICLE II

MEMBERS

SEC. 1. Any member of the A.I.M.E. of any class and in good standing may become a member of the Division upon registering in writing a desire to do so.

SEC. 2. Any member not in good standing in the A.I.M.E. shall forfeit his privileges in the Division.

ARTICLE III

DUES AND ASSESSMENTS

SEC. 1. Dues or assessments may be fixed by the Executive Committee of the Division, subject to the approval of the Board of Directors of the A.I.M.E.

SEC. 2. The funds received by the Division shall be apportioned by the Executive Committee of the Division.

ARTICLE IV

MEETINGS

SEC. 1. The Division shall meet at the same time and place as the Annual Meeting of the A.I.M.E., and at such other times and places as may be determined by the Executive Committee subject to the approval of the Board of Directors of the A.I.M.E.

SEC. 2. The annual business meeting shall be held within a few days before or after the annual business meeting of the A.I.M.E.

SEC. 3. At any meeting of the Division for which notice has been sent to the members of the Division through the regular mail at least one month in advance, a business meeting may be convened by order of the Executive Committee, and any routine business transacted not inconsistent with these Bylaws or with the Constitution or Bylaws of the A.I.M.E.

SEC. 4. For the transaction of business, the presence of a quorum of not less than 25 members of the Division shall be necessary.

ARTICLE V

OFFICERS AND GOVERNMENT

SEC. 1. The officers of the Division shall consist of a Chairman, three Vice-chairmen, Secretary and Treasurer. The office of Secretary and Treasurer may be combined in one person, if desired by the Executive Committee.

SEC. 2. The government of the affairs of the Division shall rest in an Executive Committee, in so far as is consistent with the Bylaws of the Division and the Constitution and Bylaws of the A.I.M.E.

SEC. 3. The Executive Committee shall consist of the Chairman, three Vice-chairmen, Past Chairman, and nine members, all of whom shall be nominated and elected as provided hereafter in Article VII.

SEC. 4. The Chairman and Vice-chairmen shall serve for one year each, or until their successors are elected. Each member of the Executive Committee shall serve for three years. The Chairman shall remain a voting member of the Executive Committee for one year after his term as Chairman.

SEC. 5. With the exception of the Secretary and Treasurer, no officer or member of the Executive Committee may be immediately re-elected to the same office.

SEC. 6. The Secretary and Treasurer of the Division shall be invited to meet with the Executive Committee, but without ex-officio right to vote. These officers shall be appointed annually by the Executive Committee, from the membership of the Executive Committee or otherwise.

SEC. 7. The annual term of office for officers of the Division shall start at the close of the Annual Meeting of the Institute and shall terminate at the close of the next Annual Meeting.

ARTICLE VI

COMMITTEES

SEC. 1. Standing committees, technical committees and special committees may be established, re-appointed and discharged by the Executive Committee except as provided in Article VI, Section 2.

SEC. 2. After the initial organization any technical committee may, by proper notice to the Executive Committee, elect annually its own officers and members. In the event that any such committee fails to hold annual elections, the right to reappoint or discharge shall revert to the Executive Committee.

SEC. 3. The Committee on Papers and Programs shall consist of the Chairman of the Division and of the Chairmen of the standing technical committees and of such other committees of the Division as the Executive Committee may designate.

SEC. 4. The duties of the technical committees shall be to advance the art of the industry in the field of their assignment and to secure papers within their own fields for presentation at meetings of the Division and of the A.I.M.E., subject to the regulations of the Papers and Programs Committee of the Division.

ARTICLE VII

NOMINATIONS AND ELECTION OF OFFICERS AND COMMITTEES

SEC. 1. Every year the Division shall elect a Chairman, three Vice-chairmen and three members of the Executive Committee.

SEC. 2. A Nominating Committee of five members of the Division shall be appointed by the Executive Committee immediately after the annual meeting.

SEC. 3. The Nominating Committee shall make its report to the Executive Committee not later than June 1.

SEC. 4. Any ten members of the Division may submit nominations for one or more offices to the Executive Committee not later than August 15th, and the persons so nominated shall be included in the official ballot.

SEC. 5. The voting shall be by letter ballot.

SEC. 6. The ballots shall be counted by a committee of tellers appointed by the Executive Committee.

ARTICLE VIII

AMENDMENTS

SEC. 1. Proposals to amend these Bylaws shall be made in writing to the Executive Committee and signed by at least ten members. They shall be considered by the Executive Committee and announced to the members through the columns of "Mining and Metallurgy," together with any comments or amendments made by the Executive Committee thereon. They shall be voted upon at the annual meeting of the Division in February or by letter ballot, as may be directed by the Executive Committee.

A.I.M.E. OFFICERS AND DIRECTORS

For the year ending February, 1939

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Established as a Division February 22. 1928

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Vice-chairman. H. W. GRAHAM. Pittsburgh. Pa.
Vice-chairman, THOMAS L. JOSEPH. Minneapolis. Minn.
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Secretary, LOUIS JORDAN, 29 West 39 St.. New York. N. Y.

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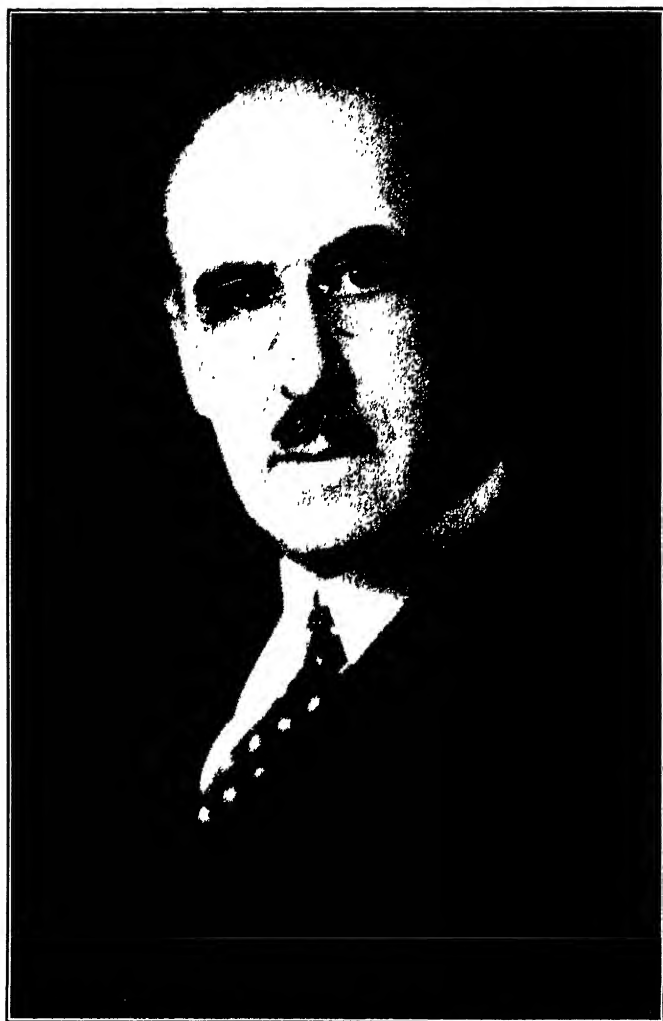
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FREDERICK MARK BECKET

Henry Marion Howe Memorial Lecturer, 1938

On the Allotropy of Stainless Steels

By Frederick Mark Becket,* Member A.I.M.E.

(Henry Marion Howe Memorial Lecture†)

Doctor Albert Sauveur, distinguished scientist and Honorary Member of this Institute, predicted in the first Howe Memorial Lecture that the privilege of delivering this annual address would be considered a highly significant honor. The intervening years have well borne out Sauveur's prophecy. I wish to assure the American Institute of Mining and Metallurgical Engineers that I also deeply appreciate this honor, recognizing at the same time the present and even more the future responsibilities with which it is accompanied.

Several of the previous lecturers had the good fortune to attend the classes of Professor Howe and to work in his laboratories. I was similarly favored, although in my instance and to my great regret the period was all too short. However, Howe's book, published in 1903, "Iron, Steel and Other Alloys," afforded me abundant opportunity to continue these studies. How well I remember the inspiration I derived from this famous book by Howe, the metallurgical master, pioneer, and educator! Remembering that Professor Howe contributed numerous papers to *The Metallographist*, a magazine supported from a technical point of view by the world's pioneers in metallography, I was curious a few days ago to learn the nature of Howe's early contributions to this magazine. The first paper by Howe in the first year of *The Metallographist* (1898) dealt with the allotropic theory; the second also treated of allotropy, and I quote the first sentence of that paper:

> The allotropic theory of the hardening of steel may, like so many other important theories, have to be accepted or rejected not on direct proof or disproof, but on the accumulation of circumstantial evidence for or against it.

Howe's ability to stimulate others by his deep understanding and clarity of expression was truly remarkable; but just as striking was his intuitive judgment concerning the implications of metallurgical data in the arts and sciences. It therefore seems fitting that this lecture comprise a broad treatment of the subject chosen, rather than a closely documented thesis on any one phase of the problem; that in it attention be focused

largely on discrete problems that present a challenge to the modern metallurgist; and that we emulate Henry Marion Howe by constructing reasonable hypotheses, even though these hypotheses necessitate some speculation and are not susceptible of rigid proof.

In this lecture the term "stainless steels" will be used in the generic rather than in the descriptive sense, and it will include all steels containing more than 11.5 per cent chromium in the iron matrix. The history of chromium and of the stainless steels has been often told, incidentally by your lecturer before the Institute of Metals Division of this Institute;[1] so the present situation concerning allotropy will be surveyed without recourse to history. However, it should be noted that throughout the lecture many of the specific examples used to show the effects of allotropic changes deal with difficulties caused by heat-treatments not suited to practical conditions, or by the imposition of temperature conditions under which the systems are unstable. It should therefore not be inferred that steels of suitable analysis properly heat-treated are subject to such short-comings. The exceptional properties of the steels of this group, such as strength, ductility, ease of fabrication and phenomenal resistance to corrosion have been described in the literature so often that repetition seems unnecessary. On the other hand, their remarkable qualities require emphasis when dealing with certain less satisfactory qualities produced under certain particular conditions.

ALLOTROPY IN GENERAL

The iron-chromium equilibrium diagram has been investigated over the entire range, and it is in a very satisfactory state up to 20 per cent or more of chromium. The implications of the gamma loop and the elimination of the gamma phase are generally appreciated. This is true also of the iron-chromium-carbon system, although to a lesser degree. The portions of the systems involving higher chromium contents still leave much for further experimentation. It is only recently that the existence of the sigma phase has been rigorously established in the iron-chromium system, and the charting of its boundaries has barely been started. This phase was described first by Bain and Griffiths[2] and given the name beta, or B, constituent. Still further, the role of austenite-forming elements has been widely investigated, and the effects of nickel with respect to the allotropic modifications of the stainless steels are fairly well understood. The effect of manganese on the allotropic changes of the iron-chromium system has received much less experimental study. There exists a rather definite concept as to the role of nitrogen as a promoter of austenite, but this concept is largely qualitative, leaving much to be learned concerning other effects of nitrogen in the stainless steels. With the foregoing statements in mind, let us now examine the allotropy of some of the indus-

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[1] References are at the end of the paper.

trial stainless steels, with special reference to the less generally recognized allotropic changes.

Many authors in the field of stainless steels prefer a categorical division of these steels into two groups: Steels essentially austenitic at room temperature, and steels either ferritic or martensitic under the same condition. While such a division makes for simplicity, increased knowledge of the allotropic changes indicates the fallacy of such a simplified point of view. Recognition of the importance of small amounts of ferrite in the so-called austenitic steels and the intentional development of steels of mixed structure have resulted in a gradual merging of the two groups. The austenitic steels commonly made today, such as the stainless steel containing 18 per cent chromium, 8 per cent nickel and less than 0.10 per cent carbon, possess a metastable rather than a stable structure at room temperature. The austenitic condition (Fig. 5), stable at the higher temperatures used for annealing, exists in the metastable state at room temperature only by reason of rapid cooling and subsequent interatomic immobility. Any condition allowing interatomic motion at once results in reversion to the more stable ferrite phase, at least locally. Such conditions may be produced either by cold work or by moderate temperature elevation, or by these factors in combination. Many of the phenomena observed as a result of cold work or heat-treatment of the austenitic steels may be explained and correlated on this basis. The mechanism of intergranular corrosion in low-carbon 18 per cent chromium, 8 per cent nickel steels is illustrative.

INTERGRANULAR CORROSION

For many years intergranular corrosion was one of the serious problems facing the stainless-steel metallurgist. Today the problem is well understood so far as prevention and cure are concerned, and indeed it might well be relegated to the sphere of academic interest. Nevertheless, as the mechanism has never been fully understood, it may be more than simply interesting to consider the phenomenon from the standpoint of allotropy.

It is generally recognized that grain-boundary conditions involve internal strain. Therefore it is not surprising that the immediate surface layers of the austenite crystals revert to ferrite, when heated to a temperature which in combination with this strain allows interatomic motion. This allotropic change in the 18 per cent chromium, 8 per cent nickel steel is accompanied by rejection of carbon in the form of carbide, owing to the lower solubility of carbon in ferrite than in austenite. The magnetic change observed by Wulff[3] and others in the crystal boundaries is substantial evidence of the nature of this mechanism. The susceptibility of 0.02 per cent carbon stainless steels is also pertinent. Finally, of further significance is the fact that the lowest temperature at which this

phenomenon occurs is not far removed from the lowest temperature at which austenite is converted to ferrite in quenched plain carbon and alloy tool steels. The common factors seem to be metastable austenite and temperature-strain condition for interatomic motion in a lattice predominantly of iron. There has been much speculation as to why the intergranular zone just described should lack the corrosion resistance to oxidizing media so characteristic of all high chromium-iron alloys. Before examining this question, it is well to review briefly the mechanism of corrosion resistance of these steels.

Evans[4] has shown that a surface film high in chromium is formed on the stainless steels, and it has been generally accepted that this surface film plays a major role in corrosion resistance. While the chromium steels are fully resistant to hot nitric acid from the industrial standpoint, it should be remembered that there is an extremely small but measurable loss in weight as a function of time. This may be explained by the theory that the film itself is attacked at a very slow rate and that the measured rate of corrosion is a combined function of the rate of solution of the film and underlying material and the rate of film formation. In oxidizing media the rate of film formation is high and the net corrosion loss is low. Plain chromium steels exhibit increased corrosion loss in reducing media, and this corrosion loss is lowered only by the addition of other elements to the chromium-iron matrix—nickel, for example.

With the foregoing concept of corrosion resistance in mind, let us consider the mechanism of intergranular corrosion. It may be assumed that the rate of formation as well as the character of the film is changed by chromium depletion in the intergranular zone, or that the rate of solution of this film and underlying metal is greatly increased because of a change of potential produced entirely by mechanical conditions. Unfortunately, the experimental difficulties in measuring local differences of potential are so great that the actual potential gradient within the intergranular zone has never been accurately determined. However, there is an interesting parallel in plain carbon steel of eutectoidal composition. A steel of this type, when quenched and tempered at various temperatures and then subjected to acid, shows markedly increased attack after tempering to that fine state of division of cementite and ferrite commonly known as troostite. This increased attack must be due to potential gradients caused by mechanical stress. This stress is produced by the precipitation of carbide particles of a critical size in the ferrite matrix, and obviously it cannot involve chromium depletion. By analogy a "troostitic" structure—iron, chromium, or other carbides dispersed in a chromium-iron matrix—is obtained in the intergranular zones of sensitized stainless steel. This can be expected to contain potential gradients due to mechanical stress, and it is natural to expect a marked increase of attack solely because of increased rate of solution of the film and underlying material.

As this action can occur without change of the formation rate or character of the film, there is no need to assume chromium depletion. The accompanying photograph (Fig. 1) might well be given the following label without exciting comment:

Austenitic stainless steels subjected to a temperature gradient from room temperature to 900° C. after high temperature quench, attacked with nitric acid.

Actually, it requires only the omission of the first two words, "austenitic stainless," to correctly describe the plain carbon steel specimen on the top. The parallel case in stainless steel is shown below the carbon steel. It should be mentioned that the carbon steel was merely etched for a moment, while the stainless steel was submerged in boiling acid for many hours. Furthermore, both in the stainless and the plain carbon steels,
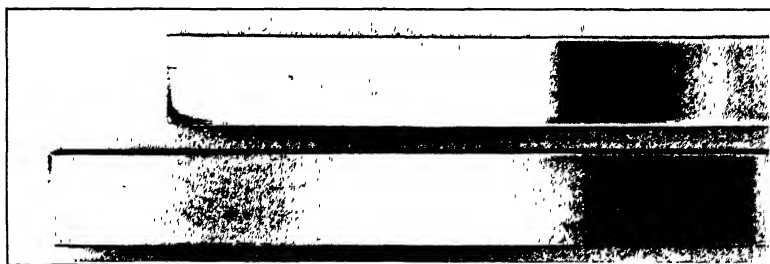
FIG. 1.—STEELS SUBJECTED TO A TEMPERATURE GRADIENT FROM ROOM TEMPERATURE TO 900° C. AFTER A HIGH-TEMPERATURE QUENCH, ATTACKED WITH NITRIC ACID SHOWING TROOSTITIC ZONE AND INTERGRANULAR ZONE.

when the temperature is elevated so that the fine carbides agglomerate the materials are no longer sensitive to the selective corrosion.

The total elimination of intergranular sensitization by the addition of suitable amounts of columbium (Fig. 2) is in keeping with the above troostitic theory of intergranular corrosion, as shown in the third specimen. The columbium eliminates effective differential solubility of the carbon in austenite and ferrite by reducing that dissolved in the austenite to a very low value, and no troostitite is formed. The intergranular resistance of stabilized titanium-bearing 18 per cent chromium, 8 per cent nickel steels may be similarly explained. Again, the facts are significant that stainless austenitic steel containing something less than 0.01 per cent carbon cannot be sensitized, whereas such steel containing as little as 0.02 per cent carbon is susceptible to intergranular sensitization. This carbon content of 0.02 per cent is ample to produce a troostitic structure. Tests show that the solutions resulting from nitric acid attack of annealed and of sensitized 18 per cent chromium, 8 per cent nickel low-carbon steels contain the same ratio of chromium to iron. All the above observations are entirely consistent with the troostitic theory of intergranular

corrosion and they emphasize the role of the allotropic transformation, austenite to ferrite, in the intergranular-corrosion phenomenon.

HOT-WORKING AND CORROSION RESISTANCE OF AUSTENITIC STEELS

Having noted the marked effect of small quantities of ferrite on intergranular corrosion, let us consider the thesis that the existence of small amounts of ferrite in the so-called austenitic steels may have an important effect when present in the matrix. Such ferrite is not usual in the plain 18 per cent chromium, 8 per cent nickel steels, but strange effects have been noted in steels of this type to which molybdenum, titanium, and columbium (singly or in combination) have been added to improve corrosion resistance without otherwise modifying the analysis. The addition
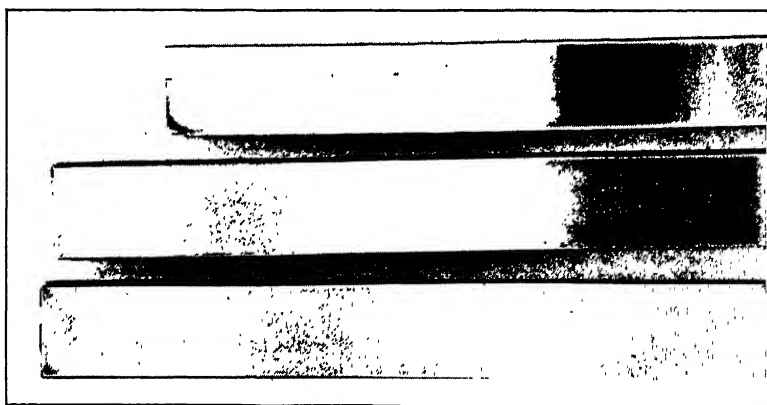
FIG. 2.—SELECTIVE ATTACK ON SPECIMENS OF STEEL SUBJECTED TO A TEMPERATURE GRADIENT AND ETCHED WITH NITRIC ACID.

Top, plain carbon steel; center, low-carbon 18-8 steel; bottom, columbium-bearing 18-8 steel (not attacked).

of ferrite-forming elements to the 18 per cent chromium, 8 per cent nickel steels requires an increase of austenite-promoting elements such as nickel and manganese to obtain satisfactory hot-working properties and maximum resistance to corrosion after certain heat-treatments.

The elements molybdenum, titanium, and columbium are all strongly ferrite-forming, and they tend to produce ferrite in the steels at room temperature by reason of two distinct mechanisms. Primarily, the structure may contain appreciable amounts of ferrite, corresponding to equilibrium at the elevated temperature from which the material is quenched or at which it is hot-worked. This corresponds to a shift in the two-phase portion of the gamma loop in the pertinent section of the diagram, which shift is dependent on the amount of the ferrite-forming elements used. Secondly, the tendency of the austenite to revert to ferrite is increased by the addition of ferrite-forming elements. Therefore, either on quenching or subsequent heating, a small but appreciable

portion of the austenite may revert to ferrite—the equilibrium state. There seems to be a direct causal connection between the presence of very small amounts of ferrite in the austenite matrix and the hot-working properties and corrosion resistance of these alloys. This may possibly be due to the difference in coefficient of expansion between ferrite and austenite, with a resulting elastic strain, which reduces the effective ductility and also sets up local potential differences.

From a practical standpoint it is necessary in many instances to establish the more completely austenitic character of the material. This is accomplished by the addition of increased amounts of austenite-promoting elements—witness, nickel and manganese. The nickel serves to produce the more completely austenitic structure by shifting equilibrium conditions at elevated temperatures and by eliminating the ferrite phase under these conditions. Manganese acts similarly. Both of these elements strongly tend to retain austenite on quenching, even at very low carbon contents. Accordingly, a moderate increase in nickel content, together with elevation of manganese to some 2 per cent, is advocated when appreciable quantities of ferrite-forming additions are made to the 18-8 type of stainless steels. This subject has not been given sufficient consideration in the past, and it is commended to the attention of the practical metallurgist in the field of stainless steels.

Steels with Two-phase Structure

In the previous section it was stated that small amounts of ferrite in the austenite matrix of stainless steels may have an adverse effect on hot-working properties and general corrosion resistance. When the proportion of ferrite with respect to austenite is increased, separate ferrite grains are clearly distinguishable, and curiously enough these ferrite grains have no deleterious effect on the hot-working properties or the corrosion resistance. The explanation may be that the presence of large amounts of both phases permits of plastic deformation with free boundary conditions, thus relieving microstrain produced in the mass as a whole. Alloys in which the two phases coexist are generally termed mixed-structure alloys. For example, 18 per cent chromium steels containing somewhat lower contents of nickel than the standard 8 per cent show both ferrite and austenite, and the spring steels developed by Luerssen and Green[5] are a case in point. This mixed structure may be produced by partially or completely eliminating the nickel and introducing manganese. Steels of this type were produced at the Union Carbide and Carbon Research Laboratories and first reported in 1930.[6]

18 Per Cent Chromium, 8 Per Cent Manganese Low-carbon Steels

Probably the best known of these steels contains about 18 per cent chromium, 8 per cent manganese, and approximately 0.10 per cent carbon.

A report on the system including them is being presented at this annual meeting by Messrs. Burgess and Forgeng[7] of the Union Carbide and Carbon Research Laboratories. The constitution of the 18 per cent chromium, 8 per cent manganese steel at 1000° C. is approximately half ferrite and half austenite, and no amount of manganese is sufficient to render the low-carbon 18 per cent chromium steels completely austenitic at this temperature (Fig. 3). As the temperature is increased, for example from 1000° to 1150° C., the ferrite phase is increased, and if the temperature is lowered beyond 700° C. the same is true. If the chromium content is increased beyond 18 per cent the proportion of ferrite also increases, and with 8 per cent manganese and 25 per cent chromium the alloys are completely ferritic. With chromium below 12.5 per cent the 8 per cent manganese alloys are entirely austenitic at 1000° C. As a full
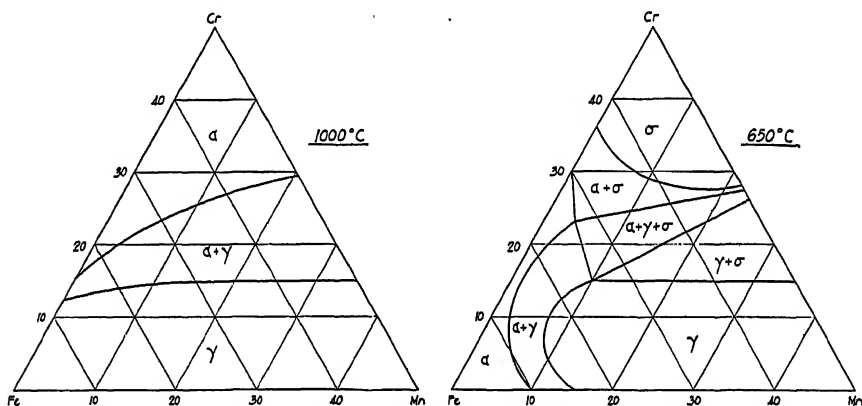
FIG. 3.—ISOTHERMAL SECTIONS OF IRON-CHROMIUM-MANGANESE SYSTEM.

discussion of this section of the phase diagram will be found in the paper by Burgess and Forgeng, it is sufficient for our purpose to emphasize the mixed structure of the alloys when given the usual annealing treatment. Of more than passing significance is the fact that these steels may be hot-rolled with relative ease, even though ferrite and austenite simultaneously exist at the rolling temperature. As might be expected, the power required is appreciably lower than that necessary for fully austenitic materials. The annealed steels are resistant to a great variety of corroding media, and measurements indicate no loss of corrosion resistance that may be attributed to the mixed structure. Other properties of these steels are readily correlated with the mixed structure. For example, cold work results in hardening to exactly the degree that might be expected from individual characteristics of the austenite and ferrite. True also it is that the physical properties of the steels are intermediate in character to the so-called fully austenitic and fully ferritic alloys. The higher manganese steels are less resistant than the higher nickel steels

when subjected to strongly reducing corroding media. The addition of copper to the chromium-manganese steels increases the corrosion resistance under these conditions. Incidentally, it contributes to the austenite retention, but there seems to be no causal relation between the corrosion resistance and the allotropy. Also, the resistance of these steels to media containing sulphur seems to be independent of allotropy. The foregoing statements are based both on laboratory tests and on observation of the behavior of appreciable tonnages produced industrially.

18 Per Cent Chromium Steels with Nickel plus Manganese at
10 Per Cent

Either nickel or manganese may be used as the austenite-promoting element in an 18 per cent chromium steel, and logically nickel and manganese may be used together for the same purpose. The steels in which the sum of the nickel and manganese is approximately 10 per cent have been investigated, and they present an interesting study in allotropy. This has more than theoretical interest in view of the resulting properties in the series. With about 6 per cent nickel and 4 per cent manganese, the 18 per cent chromium steels contain approximately 95 per cent austenite and 5 per cent ferrite in the annealed (quenched) condition. As the nickel is lowered and the manganese increased the steels contain more ferrite, and with approximately 4 per cent nickel and 6 per cent manganese they contain some 80 per cent austenite and 20 per cent ferrite, again in the annealed condition. The exact quantities of austenite to be found in these alloys are largely influenced by the carbon content, and a very few points of carbon may change these ratios appreciably. However, the noteworthy feature is that even the small amount of ferrite, about 5 per cent, found in the 6 per cent nickel, 4 per cent manganese steel is more than enough to confer freedom from the internal stress previously described, so that the behavior of the steel during both hot and cold working is exactly what would be predicted from the microstructure. Also, the corrosion resistance in the annealed condition seems entirely a function of the chemical analysis, quite independent of the allotropy; and, furthermore, the difficulties encountered in the steels containing very small amounts of ferrite are not found in the series having appreciably larger amounts. The 18 per cent chromium steels with nickel and manganese have been manufactured industrially. The following tests are of interest in connection with these statements concerning corrosion resistance and allotropy.

A number of specimens of fully annealed 18 per cent chromium, 8 per cent nickel steels, chromium-manganese-nickel steels, and chromium-manganese steels were tested for resistance to atmospheric corrosion by exposure to the industrial atmospheres of Long Island City and Niagara Falls, N. Y. Three of the smaller specimens are shown (Fig. 4) in natural

size after more than six years exposure to these atmospheres. It should be noted that the chromium-nickel steel contained practically no ferrite and 100 per cent austenite; the chromium-manganese-nickel steel contained approximately 20 per cent ferrite and 80 per cent austenite; and the chromium-manganese steel contained about 40 per cent ferrite and 60 per cent austenite. The samples were cleaned twice during exposure and once at the end of the test, merely to remove adherent foreign matter. It is evident from the photographs that there is no attack on any of these specimens. Tests on three similar steels annealed and subjected to a number of media generally considered corrosive are reported in Table 1. It is to be noted that there is no quantitative relation between allotropy and corrosion resistance.

          a   b   c
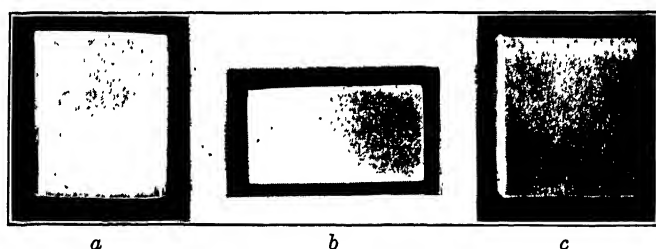
FIG. 4.—CONDITION OF WROUGHT STEEL SAMPLES (NATURAL SIZE) AFTER SIX YEARS
          EXPOSURE TO INDUSTRIAL ATMOSPHERE.

Steel	Composition, Per Cent					
	Cr	Ni	Mn	Si	C	Cu
a, Cr-Mn............................	17.70		9.40	0.57	0.07	0.68
b, Cr-Ni............................	17.90	9.04	0.40	0.40	0.10	
c, Cr-Mn-Ni........................	18.70	4.22	6.22	0.29	0.08	0.82

From the foregoing it is apparent that the two-phase alloys are comparable to single-phase alloys with respect to hot working, and further that their corrosion resistance in the annealed condition is solely a function of chemical constitution. The statements refer to annealed two-phase alloys, but in general there is a definite tendency for ferrite to form in the austenite matrix of such alloys, as a result of certain heat-treatments or of cold work. This must be given consideration in the practical application of these materials.

TWO-PHASE AND THREE-PHASE ALLOYS

Two-phase alloys obviously may be produced not only by decreasing or changing the austenite-forming elements, but also by increasing the chromium content. Thus, in the low-carbon chromium-nickel series containing 28 per cent chromium and 8 per cent nickel, a large proportion

TABLE 1.—*Corrosion Data on Chromium-nickel, Chromium-manganese and Chromium-manganese-nickel Steels*[a]

Constituent	Composition, Per Cent		
	Cr-Ni Steel Quenched from 1150° C.	Cr-Mn-Ni Steel Quenched from 1150° C.	Cr-Mn Steel Quenched from 1150° C.
Chromium..............................	17.90	17.76	17.73
Nickel........	9.04	3.83	
Manganese.............................	0.40	6.09	8.63
Silicon................................	0.40	0.47	0.54
Carbon................................	0.10	0.07	0.08
Copper................................		0.95	0.86
Ferrite................................	0.	20.	40.
Austenite..............................	100.	80.	60.

Reagent	Condition of Tests	Losses, Grams per Sq. Cm. per Hr.		
2 per cent nitric acid..........	Boiling	0.0000006	0.0000006	0.0000008
10 per cent nitric acid.........	Boiling	0.0000004	0.0000015	0.0000030
65 per cent nitric acid.........	Boiling	0.000025[b]	0.000043[b]	0.000106[b]
10 per cent sulphuric acid + 2 per cent nitric acid.........	Room Temp.	0.00006	0.0000056	0.0000011
10 per cent acetic acid........	Boiling	Nil	Nil	Nil
Acetic acid (glacial)...........	Boiling	0.000039	0.00040	0.00082
10 per cent oxalic acid........	Boiling	0.00025	0.00020	0.000145
10 per cent phosphoric acid....	Boiling	0.0000009	0.0000011	0.0000009
2 per cent lactic acid..........	Boiling	Nil	Nil	Nil
Lemon juice..................	Room Temp.	0.0000004	0.00000035	0.00000034
Orange juice.................	Room Temp.	Nil	Nil	Nil
Canned tomatoes.............	100° C.	Nil	Nil	Nil
Canned rhubarb..............	100° C.	Nil	Nil	Nil
Sulphur dioxide..............	550° C.	0.38[c]	0.13[c]	0.10[c]

[a] These three steels were selected because of their similar chromium content and were tested in each case under the same conditions at the same time by Union Carbide & Carbon Research Laboratories, Inc.

[b] Standard Huey test.

[c] Per cent loss in weight.

of ferrite will be found at 1200° C., and the alloys become fully ferritic at some 45 per cent chromium and 8 per cent nickel, again at 1200° C. As the temperature of the higher chromium alloy is lowered, the austenite is retained but the ferrite undergoes a change. This change is reversible and allotropic, the result being a new phase having the lattice of the compound FeCr. The phase is designated as sigma, and it represents the additional constituent in three-phase alloys. It is of interest to mention that as yet this phase has not been detected as a result of a change from

austenite, and it should be emphasized that its presence presupposes the existence of ferrite at higher temperatures. This extremely hard and brittle phase occupies very much less volume than the ferrite from which it is formed. Investigation of the sigma phase in the iron-chromium-nickel, iron-chromium-manganese, and iron-chromium-silicon systems has shown some surprising results. For example, Burgess and Forgeng[7] detected sigma phase in alloys with only 15 per cent chromium and 30 per cent manganese. Bain and Griffiths[2] found the sigma phase in alloys as low as 29 per cent chromium with 10 per cent nickel (Fig. 5). Jette and Andersen[8] reported the sigma phase in the iron-chromium-silicon system with chromium content as low as 15 per cent. Furthermore, crystals
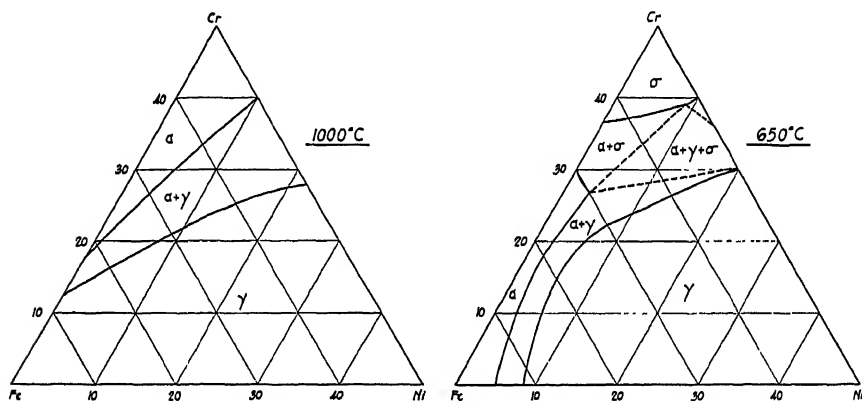
FIG. 5.—ISOTHERMAL SECTIONS OF IRON-CHROMIUM-NICKEL SYSTEM.

of the new phase cross the crystal boundaries of the ferrite from which it is formed. All this supports the concept that the brittle constituent actually corresponds to an allotropic phase, although as yet the lattice structure has not been deciphered from the X-ray pattern. Before further considering the sigma phase, it will be well to review briefly the constitution of the iron-chromium and iron-chromium-carbon systems.

IRON-CHROMIUM-CARBON SYSTEM

Consider first the effect of small amounts of carbon in the iron-chromium system. With carbon approximating zero the gamma phase disappears at about 11.5 per cent chromium; a very narrow two-phase region exists between the gamma and alpha area (Fig. 6). As the carbon increases to approximately 0.1 per cent the chromium limit for the complete austenitic phase is extended moderately to about 13 per cent, but the boundary for complete disappearance of austenite is extended to some 18 per cent chromium (Fig. 7). At 0.4 per cent carbon the boundary at which a completely austenitic structure is possible is projected to some 18 per cent, and the field of mixed structure extends well on to high

chromium contents.   For a complete discussion of this subject the reader is referred to Vol. I of the Alloys of Iron and Chromium, published under the auspices of The Engineering Foundation.[9]   It is sufficient for our purpose to point out that these steels may undergo allotropic transformations in a manner very similar to that exhibited by plain carbon steels, depending upon the presence or absence of austenite over the temperature range.   Here again is a group of stainless steels with a large number of
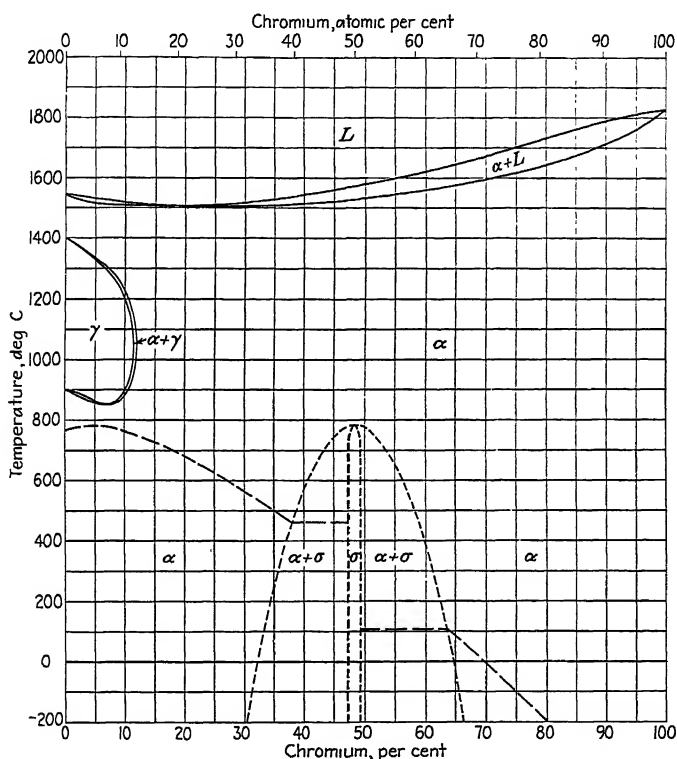
FIG. 6.—PROPOSED IRON-CHROMIUM DIAGRAM.
(Reprinted from Alloys of Iron and Chromium, **1**, 43.   Eng. Foundation Monograph.)

two-phase possibilities, and this may be further accentuated by carbon segregation in the austenite because of greater solubility in this phase.   In this category of materials are found the usual industrial steels containing 12 to 18 per cent chromium.   In the high-carbon group of steels, which behave in a manner analogous to that of ordinary high-carbon steels, the austenitic structure is complete and stable only at elevated temperatures. These steels respond to heat-treatment in the normal manner, allowing for differences in transformation rates.   These facts being well understood and often having been described in the literature, it is well to pass

at once to a group that has received less attention, the higher chromium alloys. These fall in one of the most interesting fields, that in which austenite does not appear at any temperature. Materials of this type are well illustrated by the chromium steels containing approximately 25 per cent chromium and 0.10 per cent carbon.

FIG. 7.—SECTIONS OF IRON-CHROMIUM-CARBON DIAGRAM. CONSTANT CARBON CONTENTS.

(Reprinted from Alloys of Iron and Chromium, **1**, 37. Eng. Foundation Monograph. After Tofante, Sponheuer and Bennek. *Archiv Eisenhuttenwesen*, **8**, 499–506.)

475° BRITTLENESS AND THE SIGMA PHASE

In these chromium steels another phenomenon occurs at temperatures ranging from about 400° to 490° C. The alloys undergo structural changes not microscopically discernible, which result in extreme loss of ductility at room temperature. This is not readily explainable from knowledge of the usual allotropic transformations. For want of a better

name the phenomenon has been termed "475° brittleness," generally produced by holding at this temperature for several hours. Fortunately, by rapid cooling through the embrittling range the phenomenon is practically avoided, and it is again fortunate that heating to a temperature slightly above the range completely restores the structure to the more ductile state. It should be emphasized that the material is not brittle at 475° C. and that it exhibits brittleness only at temperatures below approximately 100° C. The phenomenon just described has not been observed in chromium steels containing less than about 20 per cent chromium, although brittleness of a different nature may be developed at lower chromium contents. This composition coincides with the chromium content necessary for the second major increase in oxidation resistance of the chromium-iron series. Both phenomena imply a critical minimum chromium content in the lattice, and both involve mechanisms that depend on this critical minimum content. As superstructure formation is a mechanism that would involve such a critical minimum content, 475° brittleness may be due to a superstructure. However, the various peculiarities of the phenomenon render this hypothesis untenable at present.

Although it does seem probable that the brittleness is caused by a precipitate of submicroscopic size, investigation has yielded little as to the nature of the precipitate. The suggestion has been made that this precipitate might be the sigma phase found in the iron-chromium system,[10] as well as in many ternary systems. Accordingly an attempt has been made by Union Carbide and Carbon Research Laboratories to shed light on any relationship between the sigma phase and 475° brittleness. As this work has never been published, it will next be reported in summary.

First, consider the following facts. High-purity induction furnace alloys containing carbon as low as 0.006 and 24.35 per cent chromium exhibit 475° C. brittleness. High-purity alloys made from electrolytic chromium and electrolytic iron melted in vacuum and deoxidized with hydrogen or atomic hydrogen also exhibit 475° brittleness, and the only specimen of high-chromium iron that did not become brittle after long holding in the range had been cold-worked to strip with intermediate and final vacuum annealing.

Next, consider a series of alloys varying in chromium content from 17.8 to 58.3 per cent, with small amounts of silicon, manganese and carbon, as shown in Table 2. These were homogenized at 1000° C. and the specimens were subsequently quenched after holding at intervals from 400° to 900° C. After etching in 25 per cent hydrochloric acid in alcohol, microscopic examination under a first order red plate and polarized light permits clear differentiation between the carbides, the ferrite phase, and the sigma phase. As will be observed in the accompanying color slides

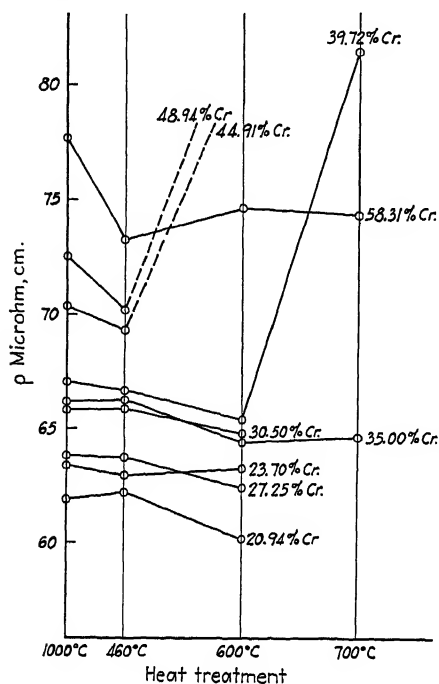(Fig. 8), the sigma phase shows alternately lemon and blue, while the ferrite remains maroon on rotation of the crossed Nicols. The results of the microscopic examination are listed in the accompanying Table 3. It should be noted that there is no well separated portion of sigma phase detectable under the microscope until the alloy contains at least 35 per cent chromium. The absence of sigma in the 58 per cent alloy is likewise pertinent. Electrical resistivity was determined on the alloys in question with results as shown in the accompanying curves (Fig. 9). The very small change in resistivity in all the alloys containing less than 40 per cent chromium, when heated to 460° after a 1000° C. quench, corresponds to a precipitation, which phenomenon is analogous to that in aluminum alloys when precipitation is first initiated. The drop in resistivity which accompanies particle agglomeration and further rejection of foreign atoms from solution is quite marked in the measurements after the 600° C. treatment of these alloys.

FIG. 9.—RESISTIVITY OF VARIOUS CHROMIUM ALLOYS HEAT-TREATED AS INDICATED AFTER 1000° C. QUENCH.

TABLE 2.—*Analyses of Iron-chromium Alloys*
USED IN 475° C. BRITTLENESS SIGMA PHASE INVESTIGATION

Heat No.	Composition, Per Cent			
	C	Cr	Mn	Si
H1	0.11	17.80	0.52	0.34
H2	0.06	20.94	0.61	0.34
H3	0.12	23.70	0.53	0.41
H4	0.10	27.25	0.63	0.37
H5	0.13	30.51	0.57	0.39
H6	0.09	31.35	0.55	0.39
H7	0.08	35.00	0.70	0.38
H8	0.12	39.72	0.62	0.38
H9	0.12	44.91	0.78	0.42
H10	0.16	48.94	0.71	0.47
H11	0.15	58.31	0.78	0.57

Fig. 8.—Effect of polarized light on color of sigma phase.
Ferrite, maroon; sigma, lemon or blue, depending upon polarization.

TABLE 3.—*Effect of Heat-treatment and Composition on Sigma-phase Formation*

Heat No.	Cr, Per Cent	Treatment	Estimated Amount of Sigma Phase, Per Cent
H7	35.0	284 hr. at 700° C., water quenched	1–2
H8	39.7	144 hr. at 800° C., water quenched	2
H8	39.7	144 hr. at 700° C., water quenched	50
H9	44.9	20 hr. at 800° C., water quenched	95–100
H9	44.9	20 hr. at 700° C., water quenched	95–100
H9	44.9	130 hr. at 600° C., water quenched	95–100
H10	48.9	144 hr. at 800° C., water quenched	95–100
H10	48.9	20 hr. at 700° C., water quenched	95–100
H10	48.9	130 hr. at 600° C., water quenched	90

The results of the hardness measurements on this series of alloys are shown in Fig. 10. The hardness peak at 475° C. is striking; it appears to
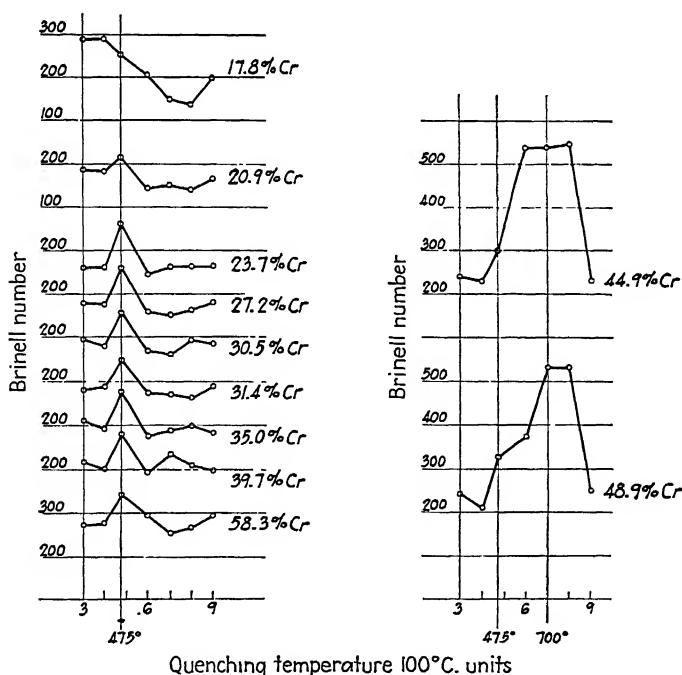

FIG. 10.—BRINELL HARDNESS OF COMMERCIAL CHROMIUM-IRON ALLOYS AFTER QUENCHING FROM INDICATED TEMPERATURES—HOLDING TIME 60 HOURS.

be independent of sigma-phase formation. The ductility tests, which fortunately were quite critical in nature, show the necessity of increasing
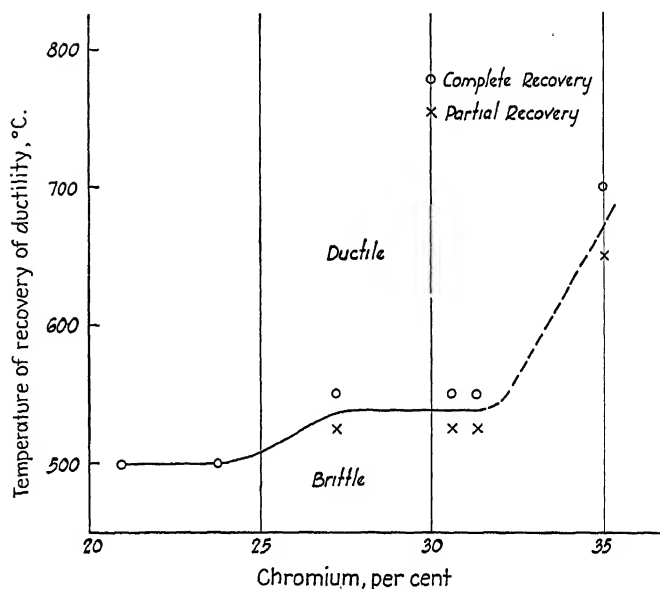
Fig. 11.—Effect of temperature on restoration of ductility of alloys previously sensitized at 475° C.
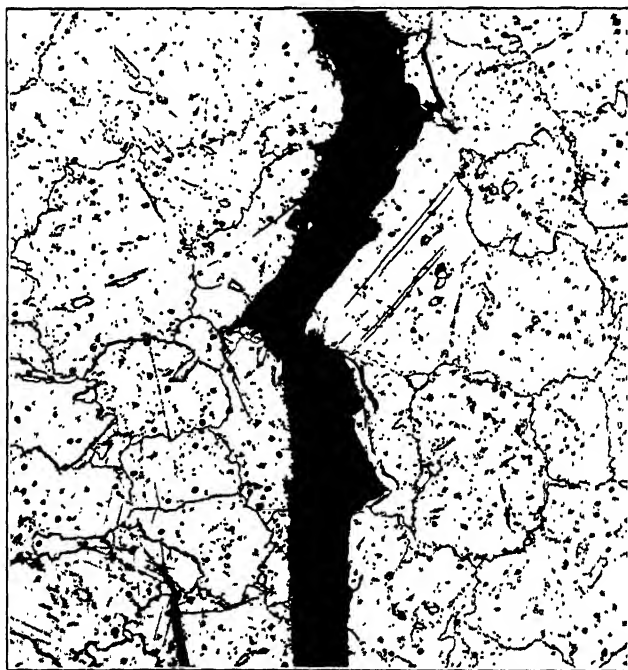

Fig. 12.—Path of fracture in chromium-iron exhibiting 475° C. brittleness. × 100.

temperature to eliminate 475° brittleness as the chromium content increases above some 24 per cent; but the curve (Fig. 11) is of the step type rather than a single continuous function, again indicating lack of correlation between sigma phase and 475° brittleness.   X-ray patterns of this series, kindly prepared for us by Dr. E. R. Jette, show the presence of sigma phase between about 37 and 55 per cent chromium.   Microscopic examination shows that the first appearance of sigma phase—that in the 35 per cent alloy—occurs at the grain boundaries.   This would be expected from our knowledge of the marked effect of strain on the rate of formation of the sigma phase.   However, the fracture of chromium-iron specimens exhibiting 475° brittleness runs through the grains and not along the grain boundaries (Fig. 12).   All these observations indicate strongly that 475° brittleness is not associated with the sigma
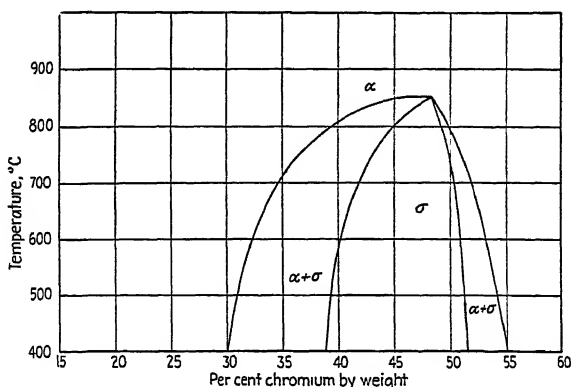

FIG. 13.—SUGGESTED DIAGRAM OF SIGMA-PHASE REGIONS IN COMMERCIAL IRON-CHROMIUM ALLOYS.

phase but that it is the result of the presence of a precipitate of unknown composition.

The need for further work on the nature of 475° brittleness is evident. The data and discussion here presented give some idea of the nature and difficulties of the problem.   It is appreciated that this work has been limited to commercial alloys and that in many instances the temperature and time of holding were insufficient to establish true equilibrium conditions.   Therefore these data cannot be used to modify the iron-chromium equilibrium diagram; but the work does suggest that the sigma phase may occur in alloys with approximately 35 to 55 per cent chromium, and a possible diagram (Fig. 13) of this region is presented for industrial guidance.

ROLE OF NITROGEN

No discussion of the allotropy of stainless steel can afford to neglect the role of nitrogen.   This element, in addition to performing a very useful function in producing and retaining a fine grain structure in chro-

mium steels, exerts a profound influence on both the ferrite-austenite and ferrite-sigma transformations. Nitrogen seems to be even more powerful than carbon in promoting and stabilizing austenite, a fact of real practical importance which is being regularly applied in industry. In common with any other stranger atoms in the chromium-rich ferrite lattice, nitrogen tends to accelerate the transformation to sigma in the alloys containing more than about 35 per cent chromium. This may be definitely inferred from the work on the existence of the sigma phase in the plain iron-chromium system. In this connection it is important to note that nitrogen in small amounts is readily absorbed from the atmosphere by the higher chromium steels at temperatures well below the solidus, so that it is invariably present to some small degree in industrial stainless steels. On the other hand, the intentional addition of larger amounts of nitrogen to stainless steels constitutes a most satisfying chapter in modern stainless-steel development.

SUMMARY

To summarize, stainless steels are based on the presence of 11.5 per cent or more of chromium in an iron matrix. In the plain chromium stainless steels containing very low carbon and chromium up to some thirty-odd per cent, ferrite is the sole allotropic phase. If the carbon increases, austenite makes its appearance at elevated temperatures and results in the usual decomposition products of austenite. When the chromium content is higher than about 20 per cent, the phenomenon of 475° brittleness makes itself evident. This is probably caused by precipitation, although the nature of the precipitate is unknown. As the chromium increases beyond some thirty-odd per cent, a new phase, sigma, makes its appearance. This phase is stable only at relatively low temperatures, and it is formed only from ferrite. Difficulties in the manufacture of plain chromium steels may be directly related to the absence of transformation, to the presence and decomposition of some austenite, or to the 475° phenomenon. Greater understanding of the equilibrium conditions and rates of reactions of phase transformations in these steels should make for more intelligent processing and application of these materials.

The introduction of austenite-forming elements results first in the formation of two-phase alloys in which the ferritic constituent decreases as the austenitic element is increased. The limits of composition and treatment resulting in the annealed two-phase structure are now appreciated, and the physical properties have been correlated with the structure. This has led to important commercial applications of these alloys, particularly in view of the fact that the corrosion resistance is independent of the allotropic state. Further increase of austenite-promoting elements in the stainless alloys results in material that is either entirely or almost

entirely austenitic at elevated temperatures, as well as at room temperature after suitable treatment. An understanding of the role of very small amounts of ferrite in these preponderantly austenitic alloys, and the correlation of this effect with working properties and corrosion resistance, is necessary to the design of new alloys free from certain phenomena now encountered. The effectiveness of columbium as a former of ferrite as well as a former of carbide is now understood; also the need is appreciated of a moderate increase in nickel and manganese when columbium, molybdenum or other ferrite-forming elements are added. It is important to remember that the sigma phase may exist in the chromium-nickel and chromium-manganese steels when the total alloy content is well in excess of the present industrial range, and the knowledge may be used to predict both favorable and unfavorable properties, depending upon the application and processing involved.

Before proceeding to the concluding paragraph, I wish to thank the members of the staff of Union Carbide and Carbon Research Laboratories who have assisted in much of the work herein reported. Particularly I wish to thank Mr. Russell Franks, metallurgist in charge of the stainless-steel group of these Laboratories, who for many years has contributed much during our efforts to advance the stainless-steel industry. Special thanks I give to Dr. A. B. Kinzel, Chief Metallurgist of the Union Carbide and Carbon Research Laboratories, for his discussion of the subject matter and assistance in the preparation of this address.

Stainless steels have made remarkable progress. This progress seems all the more remarkable if one considers the diversified industries these steels have served. How is this so? The answer is found in the intensity of research carried on with the advantages of all the modern tools of physics, chemistry, and metallurgy, together with the remarkable cooperation between the research worker, the producer of stainless steels, and the user of these materials. I should like to quote from an address I gave about seven years ago:

"Only a score of years ago chemical engineers dreamed of a material that would combine the strength and ductility of steel with the acid resistance of the ceramics. The steels with which the last hour has been spent have brought us measurably toward realization of that dream, and possibilities now dimly foreseen are pointing the way still further."

I believe it is fair to say that the accomplishments of the entire stainless-steel industry in the past several years are decidedly praiseworthy. Nevertheless, much work remains to be done so that stainless steels can be developed to serve human needs to a still greater extent.

I sincerely hope that this discussion will stimulate both the practical metallurgist and the research worker to greater efforts in connection with these complex but invaluable alloy steels. These efforts would be the ideal tribute to Henry Marion Howe.

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Trend of the Southern Pig-iron Business

By W. E. Curran,* Member A.I.M.E.

For years the geographical isolation of the Southern iron-ore district from the great producing centers in the North and East enabled it to meet its conditions and solve its own problems without regard to the practices and policies of other districts, but during the past few years distances have been shortened, practices and wages are being standardized, and these changing conditions have brought new problems to the South.

Development of Pig Iron in the South

The development of the pig-iron business in the South was very slow during its early years, gained speed rapidly in the latter part of the nineteenth century, reached its peak in 1918 and was on the decline before the depression that began in the latter part of 1929.

The first blast furnace in Alabama was built at Cedar Creek in 1818, the year before the state was admitted to the union. In 1830, Daniel Hillman was sent from Tuscaloosa to found an iron works in Roupes Valley, where rich pockets of brown ore were numerous. He built a forge on the site of what later became Tannehill furnace and called it the Roupes Valley Iron Works. There pots, pans, plows, and horseshoes were made of metal from his Catalon forge; shaped by a large hammer operated by water power. Daniel Hillman died in 1832 and the ironworks lay idle until 1836, when Col. Ninion Tannehill bought the property, rebuilt the forge and, using slave labor from his plantation, operated and enlarged the works. By 1845 he had built two crude furnaces and did a flourishing business in ovens, skillets and kettles, which found a good market all over the South.

In 1855, the plant was sold by Colonel Tannehill to Moses Stroup, an experienced ironmaster from Pennsylvania. He tore down the old furnaces and built a new plant, the ruins of which stand today (Fig. 1). This furnace plant operated continuously until it was destroyed by Northern troops in 1865. It was never rebuilt, so that the shell in the picture is the same furnace that made many tons of guns and shells for the Confederacy during the war period.

During the Civil War 16 blast furnaces were in operation in Alabama. All were destroyed by the Northern troops and some of them were never rebuilt. By 1870, some of the hardy pioneers that later dominated the iron business had begun to revive the manufacture of iron. In 1871, Birmingham was founded.

In 1876, the first coke pig iron was made by L. S. Goodrich, at Oxmoor furnace, which marked the beginning of a new era for the South. Not only many new blast furnaces but also coke ovens by the hundreds were

FIG. 1.—MASSIVE STACK OF SOLID MASONRY THAT FORMED THE SHELL OF THE TANNE-
HILL FURNACE.

built. Railroad building was given new impetus. Coal mining on a large scale was required. Ore mining developed large deposits of hard ore. During this period Col. Enoch Ensley, T. T. Hillman, James Thomas, James Shannon, James Warner, Col. Alfred Shook, Colonel Sloss, Truman Aldrich, Henry DeBardeleben, were prominent in the pioneering and development of the district.

In 1883, the Woodward Iron Co. blew in its first furnace. In 1886 and 1887, the Sloss Iron & Steel Co., the Pioneer Mining & Manufacturing Co., The Tennessee Coal, Iron & R. R. Co., and the Alabama Rolling Mills were formed. Other furnace companies were organized and millions of dollars of Wall Street capital were invested in Southern pig-iron enterprises. Fortunes were made in coal as well as in iron. In 1899, the Pioneer Mining & Manufacturing Co. was bought by the Republic Iron & Steel Co. The Tennessee company went through a period of

rapid growth and expansion. A few years later the Sloss company became the Sloss-Sheffield Steel & Iron Co. Numerous changes in ownership and personnel of the large companies and development of a number of smaller companies followed in the period from 1900 to 1910. By 1918 there were 47 blast furnaces operating in Alabama.

During the development of the pig-iron business, another great manufacturing industry began—the making of cast-iron pipe. The Dimmick Pipe Co. was founded in 1898, others followed, and the pipe industry brought more Eastern capital into the district.

During the World War period more furnaces were added and more coke ovens were built, and iron was made in anything that looked like a blast furnace. Prices skyrocketed. More coal mines were opened, by-product coke plants were built and old plants modernized. The postwar boom saw many furnaces idle. Then came the depression, with its drying up of markets, its price-cutting war for the small amount of business that existed. The depression marked the end of the road for small outlying furnace plants. Fair-weather operations, with high cost and low production, they have virtually all been dismantled. Some of them were near deposits of brown ore and when the ore was mined out it was economically impossible for them to continue. From 47 furnaces in 1918, the number has decreased to 20 in 1937.

During the business recovery since 1933 the South has lagged behind the North until within the last year. At present the demand for iron and steel in the Birmingham district is taxing the capacity of the producers.

LABOR

In the early days there was an abundance of labor in the South. Wages were whatever the producer found it necessary to pay to secure competent men. With no other industries in the field to compete for the labor, these wages were considerably lower than in the North. With the coming of other industries into the thinly populated district, the surplus of available labor was absorbed and wages began to go up. Skilled and crafts labor especially were in demand, consequently the rates paid skilled workers often equalled or surpassed the rates paid the same class in the North. The result is a labor scale covering a greater range than is found in the North. Common, or unskilled, labor takes a much lower rate in the South, but skilled operating and mechanical labor is about on an equal basis with the Northern plants. Average rates in Southern plants are 80 to 90 per cent of the rates paid in similar plants in the North. Table 1 lists some typical jobs around the blast furnace and coke plant, showing the Southern rate as 100 per cent, the Northern rate in the second column and the percentage over and under recovered typical rates for operating and mechanical work. Of the 20 rates listed,

the North is only 7 per cent higher than the South. That shows very clearly the gradual elimination of the wage differential.

TABLE 1.—*Comparison of Labor Rates in South and North*

Occupation	Percentages		
	Birming-ham	Northern Plants	+Over −Under
1. Sinter-plant operator, 2d class..................	100	111	−11
2. Sinter-plant operator, 3d class..................	100	114	−14
3. Stove tenders.................................	100	94	+ 6
4. Pig-machine operator, 2d class..................	100	98	+ 2
5. Oven heater, foreman..........................	100	84	+16
6. Oven patcher.................................	100	117	−17
7. Oven pusherman..............................	100	113	−13
8. Oven-door machine man.......................	100	114	−14
9. By-product operator, 1st class..................	100	111	−11
10. By-product operator, 2d class..................	100	105	− 5
11. Machinist, 1st class............................	100	121	−21
12. Car repairman, 1st class.......................	100	104	− 4
13. Welder, 1st class..............................	100	108	− 8
14. Carpenter, 1st class...........................	100	101	− 1
15. Brickmason, 1st class..........................	100	95	+ 5
16. Boilermaker, 1st class.........................	100	108	− 8
17. Forgeman, 1st class...........................	100	118	−18
18. Power-house attendant........................	100	116	−16
19. Locomotive-crane operator.....................	100	118	−18
20. Water tender.................................	100	96	+ 4
Averages..	100	107	− 7

RAW MATERIALS

The great deposits of iron ore, coal and limestone in the Birmingham district, all within a stone's throw of each other, have been much talked about. With cheap labor, the assembly of these materials and their conversion into pig iron was a cheap and simple operation. However, there are other facts regarding the quality of these materials, which have not been given so much publicity but which are very important.

Coking coal mined in this district is high in either ash or sulphur. It is necessary to wash it before it can be made into a satisfactory metallurgical coke. This section of the country pioneered in coal washing, and up to a few years ago produced 75 per cent of the nation's output of washed coal. Washer loss on the Mary Lee, or Big Seam, coal runs from 15 to 18 per cent in reducing its ash content to 10 per cent. Washing cost and washer loss add greatly to the cost of the finished product.

Mining costs on hard ores produced in this district are high and their iron content low. The hard ore, which makes up a large part of our furnace burden, contains 33 to 36 per cent iron; in other words, we use about three tons of ore to make one ton of iron.

While avoiding technical angles of the subject in this paper, it would be interesting at this point to make a few simple calculations on the materials used for making iron and compare with them the materials in other parts of the country. To produce a ton of pig iron from our ore it is necessary to use 3 tons of ore and about 2500 lb. of coke. This is about one ton more ore and 600 to 700 lb. more coke than is required in Northern practice. Mining, preparing and handling these extra materials necessarily calls for more man-hours per ton of iron than in the North. Southern slag volumes of 1700 to 2000 lb. per ton of iron are more than double those of Northern practice. The Southern operator blows as much wind to produce 500 tons of iron per day as the Northern operator does in producing 700 tons. Steam and utility costs are about in proportion.

This comparison shows clearly the effect of lean materials upon production cost. To offset this disadvantage, the Southern producer has had a wage differential in his favor. With this differential becoming less and less, the advantage of the South is disappearing. It is apparent that where labor represents 70 per cent of the manufacturing cost, an increase in wages will increase costs more than where labor amounts to only 50 per cent of the total cost. It is also apparent from these figures that elimination of the wage differential presents a serious problem to the producer.

But that is only one of the problems of the Southern producer. Associated with the producer is the consumer, the man who uses the iron. He was attracted to the district originally by two things—a supply of pig iron for his needs and cheap labor to convert it into pipe and other finished products. A very small amount of his product is consumed in this district. He must ship it all over the nation. Normally he produces 60 per cent of all the pressure pipe made in the United States. If he can produce it cheap enough he can meet competition in other markets in spite of the high freight rates. If his costs become too high, he will move some of his plants to other parts of the country, where he can obtain iron at the same price and produce the goods nearer market centers. So the pig-iron producer must share this problem of the foundryman and keep his price within reach of the consumer.

The same market problem that exists in other parts of the country faces the Southern producer. Unless he can keep his manufacturing cost below that of his Northern competitor he cannot retain his wide markets in the face of present and possibly increasing freight rates. Facing these changed conditions frankly, our problem resolves itself into a simple statement: If the Southern pig-iron business is to retain its place

in the nation's industry, it must continue to produce iron at a lower cost than the same iron can be produced in the North. The wage differential that has enabled us to do this in the past is on the way out. It is only a question of time until it will be entirely eliminated. New industries are arising in the South because of cheap natural gas and electric power. Old industries are moving South for the same reason. A few years ago the South claimed only 10 per cent of the nation's textile manufacturing business; today 75 per cent of all textiles produced in the United States come from the Southern States. Paper mills using slash-pine pulp are producing an ever increasing percentage of the country's paper supply. Rubber companies are on the way South with tire plants, and chemical-manufacturing plants are also being attracted by what the South has to offer. The result of this increased demand for labor will eventually bring labor rates up to the Northern levels.
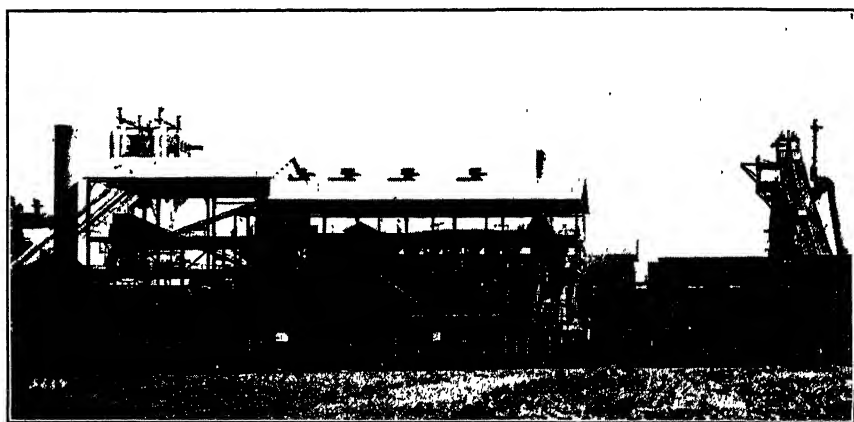
FIG. 2.—SINTERING PLANT OF REPUBLIC STEEL CORPORATION, THOMAS, ALABAMA.

The present strong demand for pig iron may make this problem seem remote, but we must be prepared to meet changed conditions should they occur. This can be done best by the development of new methods. It is our great field. Let us examine the record and note possibilities in this direction. Here are a few suggestions that command study and work.

Improvement of raw materials, both ore and coke, particularly sizing of ores, offers possibilities that we are just beginning to realize. A study of structure of coke with treatment of coal to improve physical qualities of the coke for blast-furnace use will pay dividends. Mixing of local coals with different coking characteristics offers possibilities.

Blast-furnace flue dust has long been considered a waste product. As long as coal, coke and ore were cheap there was not much incentive to try to use it. It is so high in carbon that it cannot be sintered alone, but mixed with fine ore it can be sintered, producing an excellent raw material for blast-furnace use.

The sintering plant of the Republic Steel Corporation at Thomas is wide open—not housed in on the side at all (Fig. 2). The climate makes that possible. The plant has been in operation about a year and has been very successful.

Our high-phosphorus ores have given Southern iron one characteristic that distinguishes it from other merchant iron. This high-phosphorus pig iron carries a price differential, selling below low-phosphorus iron produced in other districts. Yet for some purposes the Southern iron is better suited than the iron lower in phosphorus. We should work to convert this high phosphorus from a liability into an asset. Some of us will live to see the day when a premium will be paid for our high-phosphorus iron.

PRODUCTS

The improvement in quality of merchant iron has already been given much publicity, but there will be further improvements, for perfection has not been reached. Quality studies are with us always—and rightly so.

The product offering greatest possibilities is blast-furnace slag. In Europe, and more recently in this country, much study has been given to turning slag into higher priced products. Its use in the South has not reached very high-priced markets. We should be especially interested in developing new products and markets for slag, since our production is so high. As an example of one means of disposal recently developed, one of the local producers has added equipment to make a dry granulated slag, called Superock, for use as a light-weight concrete aggregate. A photograph of the plant and one of the Superock itself are given in a paper by J. M. Hassler.[1] In addition to its use in construction work, Superock also has value for insulation purposes.

These suggestions are only a beginning. It is our problem to keep abreast of the march of time and develop new methods and new equipment to increase efficiency and decrease man power.

CONCLUSION

If the pig-iron business in the South is to follow the upward swing of the trend curve of all business, in spite of the loss of certain natural advantages which we inherited, it can only be through developments that have not yet been made. We must study materials, methods, men and markets, for they all have possibilities that we have not fully realized. We must face the changed and changing conditions with a determination to overcome the handicap of low-grade materials and to offset the increased labor rates by new economies, new processes and a new assurance that *it can be done.*

[1] J. M. Hassler: Offsetting Increased Labor Cost in Southern Blast-furnace Operation. *Trans.* A.I.M.E. (1937) **125**, 47.

The Sintering Process and Some Recent Developments

By John E. Greenawalt,* Member A.I.M.E.

In view of the increasing importance of sintering in the beneficiation of iron ores preparatory to their reduction in the blast furnace, the writer believes the time is opportune for an up-to-date, though brief, discussion of the general principles of sintering, as well as a discussion of some of the recent improvements and mechanical developments that have been achieved in this industry, its present trend and future possibilities.

Sintering may be defined as the agglomeration of fine mineral particles into a porous mass by incipient fusion caused by heat produced by combustion within the mass itself. Its first successful application, in connection with the treatment of lead sulphide ores, was known as blast roasting. In this process the lead ore was given a preliminary roasting in a reverberatory furnace, then the incandescent mass was placed in a pot with a grate and an updraft was applied. It was soon discovered that much better results were obtained by cooling the ore, moistening it, and placing it upon an incandescent layer of fuel previously placed upon a grate, and then applying the updraft blast of air until the charge was converted into a more or less agglomerated mass. The fuel was sulphur and the process one of desulphurization, which was the principal result desired.

The application of downdraft to blast roasting brought about tremendous results; the principal one of which was that an air blast of high pressure could be passed through a layer of ore deposited on a grate, or on a grate covered by a layer of coarse porous material, without disturbing the particles of which the layer is composed. The air current is compelled to filter through the pores of the charge, whereas if the same pressure applied to the top surface of the charge with downdraft were applied to the bottom of the charge with updraft, the charge would be completely blown off the grate. Another result of reversing the draft was that a flame could readily be applied to the top surface of the charge for igniting purposes.

Broadly speaking, sintering is an oxidizing or burning process, therefore the volume of air passing through the charge is the all-important factor. The air must pass through with sufficient rapidity to produce the necessary heat, and if sufficiently rapid the combustion will take place

with a blowpipe action that will quickly generate a sintering temperature, whereas if the flow of air is insufficient, the burning will be like that of burning punk and sufficient heat will not be generated to form sinter.

The first condition, then, is to pass the air through the charge in sufficient volume to produce a sintering temperature in the mass, and this is greatly influenced by two important factors: (1) the porosity of the charge itself and (2) the pressure applied to force the air current through the pores of the charge by means of suction.

POROSITY

The porosity of the charge is influenced by the following three important factors: (1) moisture, (2) returning part of sintered charge as "returned fines," (3) mixing the charge.

Moisture.—Were it not for the fact that moisture added to fine ores increases the porosity of the charge enormously, the sintering process as applied today would be a complete failure. The porosity of fine, dry ore is so small that it becomes impracticable to pass air through the charge in sufficient volume to produce a sintering temperature. Fortunately, however, if 4 per cent of water is added to this same charge and mixed thoroughly, the porosity is greatly increased, and if we continue to add water one per cent at a time and test the porosity after each addition, the porosity of the charge will increase progressively until a maximum has been reached; then, if we continue to add water, the porosity will decrease until it has been completely destroyed. The amount of moisture used to obtain maximum porosity is usually the best percentage of water to use in preparing the charge for sintering. In actual practice, this depends upon the character of the ore and may vary from 5 to 12 per cent, not including combined moisture. Magnetic ores require the least and clayey ores the most to produce the best physical condition for sintering. The character of the sinter can be slightly influenced by the moisture content of the charge; the drier charges tend to produce a more fragile sinter and wetter charges a stronger and denser sinter. High moisture in the charge decreases its combustibility and increases ignition difficulties.

Returning Part of Previously Sintered Charge in Form of "Returned Fines."—It is impracticable to produce 100 per cent sinter in one operation, so the sintered charge is passed over a screen and all the fine material below a fixed size is returned and resintered. The size of this screen may vary from $\frac{1}{4}$ to $\frac{3}{4}$ in. and the amount returned may vary from 20 per cent to as much as 50 per cent, although in the intermittent system this is rarely more than 25 per cent. Much of this material has been sintered, so the addition of it to the charge greatly increases its porosity and sintering qualities, and thereby increases the capacity of the sintering unit. It improves the sintering charge just as sinter improves the blast-furnace charge. This practice, however, has the disadvantage of double sinter-

ing, requiring additional fuel, which adds considerably to the cost of sintering low-grade ores. This resintering of part of the charge that previously has been partly sintered, and which fuses far more readily than the original charge, strongly tends to the formation of the undesirable iron silicates in the finished sinter, so that the modern tendency is to reduce the returns to a minimum.

Preparing Charge to Consist of a Mixture of Materials, Some of Which Are Coarse and of Great Permeability.—This method of increasing the porosity of the sintering charge is very desirable whenever it can be applied—as, for example, mixing fine ores with flue dust, roll scale, etc. It is also advantageous to mix fine magnetic concentrate with coarser ores in the preparation of the sintering charge. Obviously, this method of increasing the porosity of the charge has its limitations in the materials available.

FORCING AIR CURRENT THROUGH CHARGE

Having prepared the charge so as to obtain the maximum porosity, we find a definite resistance to the flow of air through the charge. The amount of air that will flow through the charge is proportional to the thickness of the charge and to the suction applied to the lower side of the charge. The thickness of the charge treated is very important. In plants using the intermittent system, the depth of the charge varies from 7 in. with a fine magnetic concentrate to 18 in. with the fines below $\frac{3}{8}$ in. of a hematite ore. Economically, a thick charge has many advantages over a thin layer. The cost of igniting and charging a thick layer is no more than that of a thin layer, and it also has the advantage of requiring less sintering fuel. The time of sintering—that is, the time required for the sintering zone to travel from the top surface of the charge to the grate—varies from 10 to 18 min. Experience has shown that 18 min. should be the maximum, for the reason that if a charge requires more time than this to sinter the portion of the charge near the grate dries out and greatly slows up the travel of the sintering zone through the charge. The sintering zone should travel through the charge at the rate of about 1 in. per min. Some years ago, at Sparrow's Point, a wet, clayey ore was mixed with fuel in a revolving drier; it came out in balls the size of marbles having considerable strength and these marbles then were successfully sintered in a charge 56 in. thick.

The thickness of the charge is also dependent upon the suction available. For some years, in connection with the intermittent system, we have been advocating and using powerful fan exhausters capable of giving a suction of 50 in. of water, and from the results obtained the writer is convinced that the use of high suction in the future will become more and more the accepted practice. This is especially true for sintering at a low cost large tonnages of ores with reduced fuel consumption, and

thereby eliminating almost completely the possibility of forming iron silicates in the finished sinter.

Fig. 1 is a chart based upon the tests made by A. K. Walter, and illustrates clearly the positive results that can be obtained by applying increased suction to a sintering apparatus. Here are represented the results obtained with a series of tests made from a large amount of ore prepared for this purpose, so as to have uniformity in fuel and moisture. This large charge was thoroughly mixed so that the small individual charges taken from it were as nearly alike as possible except for the suction
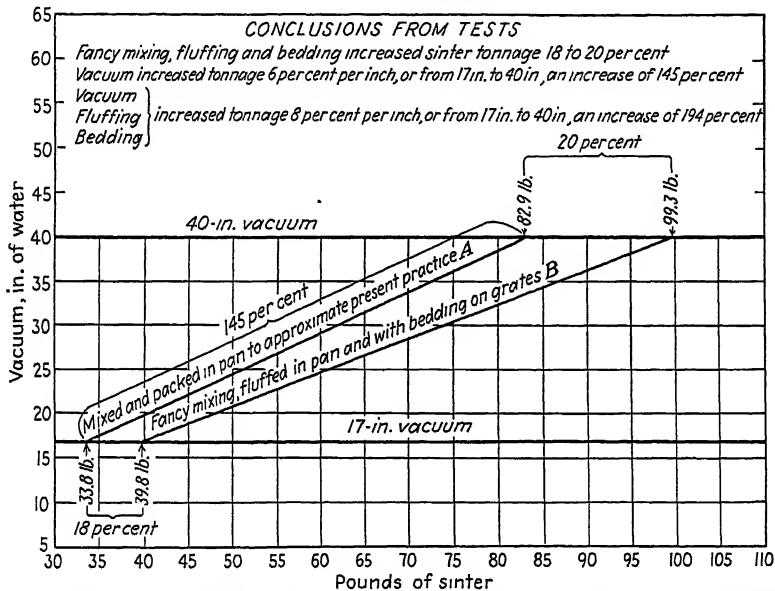
FIG. 1.—RESULTS OBTAINED BY APPLYING INCREASED SUCTION TO SINTERING APPARATUS.
Based on tests by A. K. Walter.

applied to the charge. Vertical distance on the chart represents the suction and the horizontal distance the number of pounds of sinter produced. Line A represents the sinter produced by shoveling the charge directly into the pan with more or less irregular packing, line B represents the production obtained by carefully fluffing the charge so as to give it the greatest amount of porosity possible and the greatest amount of uniformity. Notice that with 17 in. of suction, the increase in sinter production due to proper charging was 18 per cent while with 40-in. suction, the increase was 20 per cent. By increasing the suction from 17 to 40 in., the capacity was increased 145 per cent, and by increasing the suction from 17 to 40 in., and at the same time depositing the charge into the sintering apparatus with the greatest amount of uniformity and porosity, the capacity was increased 194 per cent. In other words, for

every inch of increase in suction, there was an increase in sintering capacity of 6 per cent in the first case and of 8 per cent in the second case. This pronounced increase in capacity has been fully demonstrated on a large scale in practice.

To apply high suction, it is obvious that the sintering apparatus must be airtight from the top surface of the charge to the fan exhauster, and that exhaust fans of superior design are required. High-suction fans, when carefully designed and properly constructed, are capable of operating over long periods of time without attention except lubrication. At one plant, the exhausters capable of producing 50 in. of water suction were in use for over a year without repairs of any kind, and at another plant for over two years without repairs. This is a real accomplishment, when we consider that the tip speed of the impellers is over 26,000 ft. per min. The successful operation of these exhausters is due to accurate balancing of the impeller and thorough protection of the impeller from heavy dust by means of a carefully constructed grate for supporting the charge and an efficient dust catcher between the exhauster and pan.

ESSENTIALS IN PROCESS

Proper ignition of the charge is important, and the time required to accomplish this should not exceed 30 sec. Every square inch of the charge surface must be evenly and fully ignited. Long exposure of the igniting surface to flame dries out the charge and produces uneven sintering. A clean, high temperature and highly oxidizing flame applied instantaneously to every square inch of surface produces the best results. For this reason, it is preferable to use high-grade fuel such as oil or natural or coke-oven gas instead of blast-furnace or produced gas.

In any downdraft sintering apparatus, the grate receives severe punishment. It should be self-cleaning and have an opening amounting to at least 20 per cent of the total grate area. The amount of grate opening, however, depends upon the character of the material being sintered. Fine ores lacking in cohesiveness are readily drawn through the grate by the air blast, and therefore require a grate with smaller opening. Whenever possible, it is advisable to place a thin layer of coarse material upon the grate, and when sintering fine ores, it is excellent practice to deposit a layer of the ore upon the grate without the admixture of fuel or very little fuel, as this prevents the formation of highly fused sinter, which frequently forms next to the grate.

Sinter should be air-cooled, for the reason that if red hot sinter is doused with water it becomes very brittle and breaks up easily when handled. Air-cooled sinter is much stronger than water-cooled sinter, and sinter made from a charge containing lime should not be moistened.

Sulphur elimination is of vital importance in the preparation of certain sulphur-bearing iron ores, and this element should be reduced to

0.10 per cent or less for use in the blast furnace.   The all-important point
to remember in sulphur elimination is to reduce the carbon content of the
charge to a minimum, so that the heat released by the combined burning
of the carbon and sulphur is just sufficient to produce a sintering tempera-
ture.   If more carbon is present, the oxygen combines with the carbon in
preference to the sulphur, thus fusing some of the sulphur compounds
from which it is extremely difficult to remove the sulphur.   The extreme
sensitiveness of this action is shown by Table 1.   Notice that increasing
the coke from 2.43 to 2.90 per cent increased the sulphur in the sinter
0.01 per cent with material crushed to $\frac{1}{4}$ in., and with material crushed
through $\frac{5}{16}$-in. screen the sulphur in the sinter increased from 0.09 to
0.13 per cent.   Fine crushing also favorably affects sulphur elimination.

TABLE 1.—*Results Obtained in Sintering Tests Made with Siderite
Ore Containing 2 Per Cent of Sulphur*

Ore Size, In.	Coke, Per Cent	Iron, Per Cent	Sulphur, Per Cent
Below:			
$\frac{1}{4}$.............	2.90	51.84	0.10
$\frac{1}{4}$.............	2.43	51.64	0.09
$\frac{5}{16}$.............	2.90	52.04	0.13
$\frac{5}{16}$.............	2.43	52.04	0.09

Coke breeze crushed to pass a 10-mesh screen is an excellent fuel for
mixing with the charge to be sintered, and another satisfactory fuel is
anthracite culm.   Bituminous coal is not satisfactory because of its
volatile constituents; these are not only wasted but tarry compounds are
condensed and clog the pores of the charge, greatly interfering with the
flow of air through the charge.   To obtain uniform distribution through-
out the charge and avoid intense local temperatures, the fuel must be
finely divided.   There is not sufficient time to burn large particles of
fuel, therefore the unburned fuel is wasted so far as the sintering operation
is concerned.   Ores containing 6 per cent sulphur have sufficient fuel to
produce a sintering temperature.   Blast-furnace flue dust always has an
excess of fuel for sintering; in fact, a ton of dust with 15 per cent of
carbon has sufficient fuel to sinter $3\frac{1}{2}$ tons additional of fine ore or
concentrate providing the charge is properly arranged and treated with
high suction.

The object of sintering material is to prepare it for treatment in the
blast furnace, therefore the chemical and physical qualities of the sinter
are of major importance.   Only during the last few years has the full
significance of the fact that sinter may be good, bad or indifferent in the
blast furnace been fully appreciated.   The writer has been confused many
times by conflicting reports regarding the effect of sinter in the blast

furnace, and well remembers being told frequently that one cannot use more than 18 per cent sinter in the furnace without difficulty, for the reason that the sintered material melted and reached the tuyere zone without reduction. Other reports were that sinter could be used in much greater quantities and the results were most excellent. In the early days of sintering, the sole object was agglomeration. In fact, many authorities considered it necessary and desirable to form iron silicates in order to make a sufficiently strong sinter. For example, Schwartz contends[1] that the strength of sinter was increased by the presence of silica that was converted into iron silicate. In recent years, the opinion has been gaining ground that a highly fused sinter charged with iron silicates is not the best sinter for blast-furnace purposes, and this was conclusively demonstrated in the very excellent paper by Agnew.[2] The solution presented was the elimination of the silica before sintering, but obviously this can be accomplished only with a limited class of materials.

The problem then becomes one of converting all kinds of ores into a sufficiently strong sinter for blast-furnace use without the formation of iron silicates. The factors involved in the avoidance of iron silicates are the control of the temperature at which sintering occurs and the time the charge is exposed to this temperature, the amount of returned fines in the charge and probably the presence of small quantities of basic materials in the charge.

SINTER FROM RED HEMATITE ORE

By means of high suction and an improved arrangement of the charge to be referred to later, the writer has obtained some rather remarkable results in sintering fine red hematite ore. Sinter sufficiently strong for blast-furnace purposes was repeatedly produced with 3.5 per cent coke in the charge, and also excellent sinter was made by adding 16 per cent flue dust, so that the charge sintered contained only 2.84 per cent carbon. This is considerably less than one-half the amount of fuel required heretofore for sintering this ore. The fines below $\frac{1}{4}$ in. amounted to 20 per cent, and were returned to the succeeding charge, and a 16-in. charge was sintered in 15 minutes.

The following is the analysis of the fines from which sinter was made, with 3.5 per cent coke breeze for the microscopic investigation: SiO_2, 12.32 per cent; Al_2O_3, 3.47; CaO, 16.75; MgO, 0.51; Fe, 36.35; P, 0.30; Mn, 0.17; H_2O, 2.74; total, 72.61 per cent.

The microscopic examination of this sinter was made by Prof. Paul F. Kerr, of Columbia University, to whom the writer is indebted for this very interesting study. The material was impregnated with Bakelite for

[1] G. M. Schwartz: Iron-ore Sinter. *Trans.* A.I.M.E. (1929) **84,** 39.

[2] C. E. Agnew: Benefits from the Use of High-iron Concentrates in a Blast Furnace. This volume, page 116.

the preparation of polished surfaces, and with balsam for the preparation of thin sections. In this way, suitable mounts were prepared for various types of microscopic examinations.

Fig. 2 is a photomicrograph showing crystals of hematite and magnetite embedded in glass, as they appear on a polished surface. The metallic constituents of the sinter occur either as magnetite or hematite. The magnetite occurs as a recrystallization product of the original hematite in clusters of minute octahedral crystals. The original fine
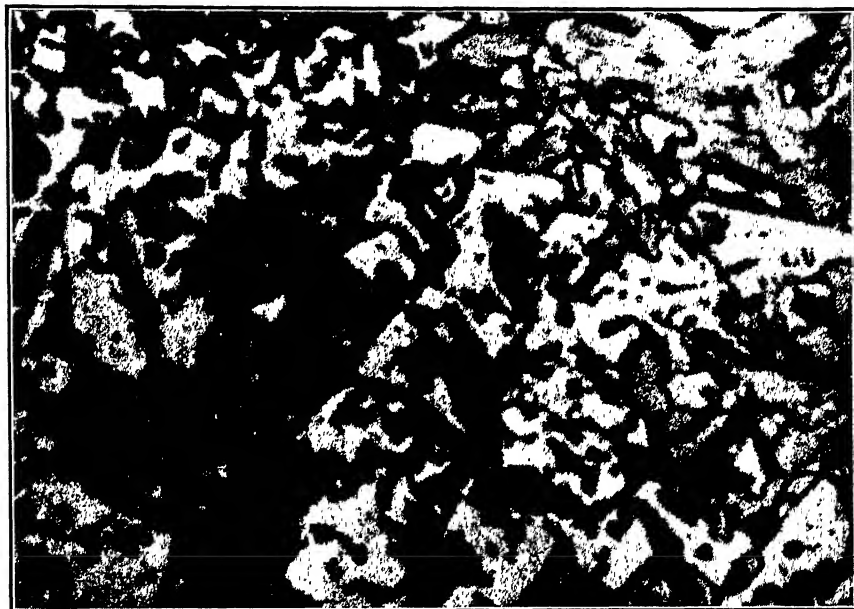
FIG. 2.—CRYSTALS OF HEMATITE AND MAGNETITE EMBEDDED IN GLASS, AS THEY APPEAR ON A POLISHED SURFACE.
Large, light gray angular areas represent hematite crystals in reflected light. A few dendritic groups of magnetite crystals are shown at the side.

hematite powder has been recrystallized in clusters of minute, sharply defined, hexagonal crystals of the same mineral.

Contrary to the generally accepted opinion, Professor Kerr has shown that the iron oxide present in the sinter is not nearly all magnetite. He shows that all the hematite present in the original ore has been changed partly into magnetite and partly into a recrystallized form of hematite. This conclusion is substantiated by results obtained in a large sintering plant where the sinter was dumped into a pit with the intention of lifting it from the pit by means of a powerful magnet. Only a comparatively small proportion of the sinter was lifted by the magnet.

The principal nonmetallic constituents of the sinter, produced during the heat-treatment, is glass. Apparently the fine quartz particles in the

original ore, together with a considerable proportion of the calcite, form glass. The brownish color would indicate a contamination with iron. This glass formation is clearly shown in Fig. 3.

Fig. 3 also shows skeleton crystals of magnetite as they appear on a polished surface. The edges of the crystals are much more prominently developed than the crystal faces or the interiors. The skeleton outlines are embedded in glass, and glass even fills the interior of some of the crystals.

The microscopic investigation showed that this sintered product contained no pure iron silicate, so it was decided to make a similar study

FIG. 3.—SKELETON CRYSTALS OF MAGNETITE EMBEDDED IN GLASS.

of sinter produced from an ore of high-silica content under the same conditions of high suction and low fuel content. The tendency to form iron silicates should certainly make its appearance with a charge of this character. For this purpose, a sinter made from ferruginous sandstone of the following composition was selected: Fe, 24.48 per cent; P, 0.035; SiO_2, 57.62; Al_2O_3, 4.57; total, 97.195 per cent. To this charge was added 24.2 per cent flue dust containing 18 per cent carbon and 10 per cent lime, or 1.95 per cent CaO in the charge. This charge was sintered with 50 in. of water suction.

The following is quoted from Professor Kerr's report:

"Fig. 4 is a photomicrograph showing the association of quartz and unaltered iron ore. Powdery hematite is seen coating the grain of quartz

and filling the fractures. The dark mineral surrounding the grain is magnetite.

"Fig. 5 is a photomicrograph showing the general relationship of the minerals in the sintered iron ore. The quartz grains (light colored areas) are set in a cementing medium composed of iron and glass.

"A summary of the complete microscropic study of this sintered ferruginous sandstone indicates that the following constituents are present:

FIG. 4.—QUARTZ AND UNALTERED IRON ORE.
Powdery hematite coats the grain of quartz and fills the fractures.

"*Metallic.*—Magnetite occurs in minute crystals of from four to six sides, and is a recrystallization product of the original hematite. Hematite occurs in minute hexagonal crystals, which are recrystallized from the original iron ore. It also occurs as a fine powder, which is residual from the original state.

"*Nonmetallic.*—Quartz, a large part of the grains of which are residual from the original ore, and still coated, in many cases, with powdery original hematite. In some cases, fusion has taken place just around the edge of the grain, and as a result, the grains are rimmed with a glass ring. Glass, of a basic nature, acting as an embedding medium for the iron constituents of the sinter. Zircon, in a few scattered grains. Zircon is a refractory mineral and is probably an unaltered constituent of the

original ore.   Carbonate, which occurs in a few minute and widely scattered grains.

"Examination of the sinter, both in thin section, and on polished surface, indicates that there is no silicate of iron present.   It appears that the conditions of time and temperature to which the original ore was subjected in the process of sintering were not quite sufficient to permit formation of silicate of iron.   Either the time may have been too short or the temperature may have been too low to bring about this recrystalliza-

FIG. 5.—GENERAL RELATIONSHIP OF MINERALS IN SINTERED IRON ORE.
Quartz grain (light colored) set in cementing medium of iron and glass.

tion.   Original hematite in the final product and comparatively slight alteration of many quartz grains are significant."

SINTER IN BLAST-FURNACE CHARGE

These studies have demonstrated a fact that may have great practical importance; i.e., that lime and other bases of the charge combine with the silica under the conditions existing in a sintering charge at a temperature below that of iron silicate formation, and would indicate that the work of the blast furnace could be advanced by the sintering process without interfering with the reducibility of the iron components of the charge, and that sufficient lime should be added to the sintering charge to produce a self-fluxing sinter.

Fig. 6 is a photograph of two sinters made from the same ore and with the same suction of 50 in. of water. The sinter to the right was made with 3.5 per cent coke, and is an ideal product for the blast furnace, completely free from iron silicates. Notice its great porosity and the thinness of the walls of its cellular structure, also that incipient fusion only was attained, and not a smelting temperature. The sinter to the left had more return fines and 4.5 per cent coke. Here a pronounced smelting or slagging action is observable, more so in the original sample than in the photograph. This sinter is fused entirely too much for the most economical
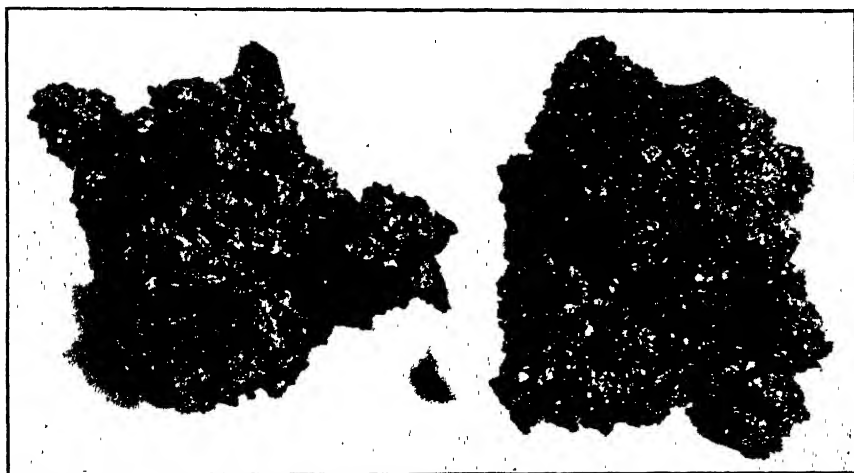
FIG. 6.—TWO SINTERS MADE FROM SAME ORE WITH SUCTION OF 50 INCHES OF WATER.

results in the blast furnace. The extreme sensitiveness of sintering charges to fuel under high suction is again clearly illustrated by these two exhibits—one charge having only one per cent more coke than the other.

HIGH THERMAL EFFICIENCY IN SINTERING

A discussion of sintering would not be complete without calling attention to the extraordinarily high thermal efficiency of this process when properly conducted. From the thermal point of view, it may well rank as the most efficient process in the entire metallurgical field. Let us consider the siderite ore to which we have referred previously. This charge contained only 2.43 per cent coke, plus 2 per cent sulphur as combustible, and yet there was sufficient heat to bring the entire mass to the point of incipient fusion, drive out all the water in the charge, and eliminate 31.56 per cent CO_2, the latter being an endothermic reaction. This is also true of the hematite ore where 3.5 per cent coke was sufficient to sinter the charge and eliminate about 12 per cent CO_2.

If we examine carefully the conditions existing in a charge undergoing sintering, we can readily discover the reason for this efficiency. Suppose

we consider a sintering charge about 16 in. thick deposited in an inter-
mittent sintering unit. The igniting flame is applied instantaneously to
every square inch of the top surface and maintained for about 30 sec.
The sintering zone then moves downward in a plane whose area is the size
of the entire sintering unit and parallel to the grate surface. This
sintering zone—that is, the zone where the actual sintering occurs—is
very thin, probably never more than $\frac{1}{16}$ in. in thickness. Immediately
after ignition, this zone passes beneath the surface, and after that, the
incoming air, before reaching the sintering zone, must pass through
incandescent sinter, so that by the time the air reaches the sintering zone
it is in a highly heated condition. On the other side of the sintering zone
are the highly heated products of combustion passing through the part
of the charge immediately ahead of the sinter zone. So there is not only
preheated air, but a highly preheated charge, thus producing excellent
conditions for economical combustion. Again the products of combus-
tion are filtered through the pores of the charge in a downward direction,
so that their heat is quickly transferred to the charge and remains within
the charge. The effectiveness of this principle is illustrated by a curve
representing the temperature of the gases directly after leaving the charge
taken at frequent intervals. In a large number of tests, the temperature
of the gases were checked by pyrometer readings, and these were quite
uniform for the first 4 or 5 min. around 120° to 130° F. It then gradu-
ally rose and leveled off at 160° to 165° F. This temperature persisted
until toward the end of the run, when it rose abruptly to 650° to 700°,
after which it receded as the fuel of the charge was burned out. The peak
of the temperature curve indicated the arrival of the sintering zone at the
grate surface, and after this nothing was gained by continuing the air
blast through the charge. It is interesting to note that for 13 of the
15 min. required for sintering the gases were below the boiling point
of water.

To obtain the fuel economy referred to, it is necessary to properly
arrange the charge undergoing sintering, and this depends upon the
discovery that, while treating a charge with high suction, a sintering
temperature once properly initiated by means of a thin top layer contain-
ing the necessary fuel can be maintained and propagated through a charge
containing much less fuel than that necessary to start or initiate that
sintering temperature. For example, the charge may consist of a layer
$14\frac{1}{2}$ in. thick having mixed with it 3 per cent of coke, upon which is
placed another layer $1\frac{1}{2}$ in. containing 6 per cent coke, thus forming a
charge 16 in. thick. The top layer after igniting is quickly brought to a
sintering temperature, which is rapidly communicated to the charge
beneath, which contains only 3 per cent fuel, and thereby initiates a sinter-
ing temperature in this part of the charge; this sintering temperature is
transmitted and propagated to the portion of the charge directly beneath

it, and so on until the entire charge has been sintered. By reducing the fuel content of the main charge below that ordinarily used, the sintering action is speeded up so that the heat required for sintering does not remain long enough in any locality in the charge to cause the formation of iron silicates.

The proper application of the igniting flame is also a contributory factor in attaining the requisite fuel economy, and the improved method of high-temperature ignition is shown in Fig. 7. The drawing shows an ignition hood equipped with two burners operated by electric motors at 3600 r.p.m., and can be adapted for oil or gas. The fuel is fed near the center of the wheel and when oil is used it is completely atomized and mixed with the necessary amount of air so that combustion is practically
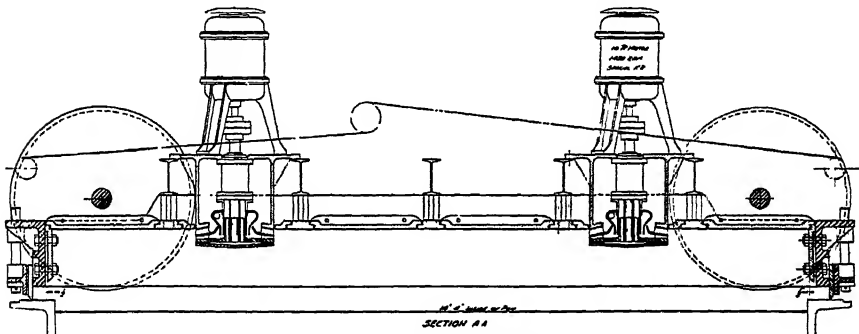
FIG. 7.—IMPROVED METHOD OF HIGH-TEMPERATURE IGNITION.

instantaneous and high heat is generated. The swirling action of the flame prevents hot spots and produces a uniform temperature at all points of the surface. As applied to the intermittent system, this method of igniting is far superior to any other method previously used.

IMPORTANT FACTORS

Fig. 8 represents the automatic, self-cleaning grate, which has been very successful in practical operation, giving a clean grate for every charge sintered. The grates, actuated by means of a heavy sliding weight, are given a differential movement, one-half of the bars moving up ½ in. and the other alternate bars moving down ½ in. during the first half revolution of the pan; during the second half of the revolution, these are brought back into normal position ready to receive a fresh charge.

The method of mounting the bars is clearly shown in Fig. 9. Here are shown the yokes upon which the bars are mounted, and the way in which the yokes are connected with the sliding weight. One set of bars across the pan is mounted on one side of the yoke and the adjacent row of bars on the other. The movement of the sliding weight (about 4 in.) moves the yoke, thereby producing the differential movement between the bars.

The bars overlap at the ends and the distance between them can be accurately maintained so that the grate opening also can be definitely maintained. This opening is generally $\frac{5}{16}$ in., or 23.8 per cent of the grate surface.
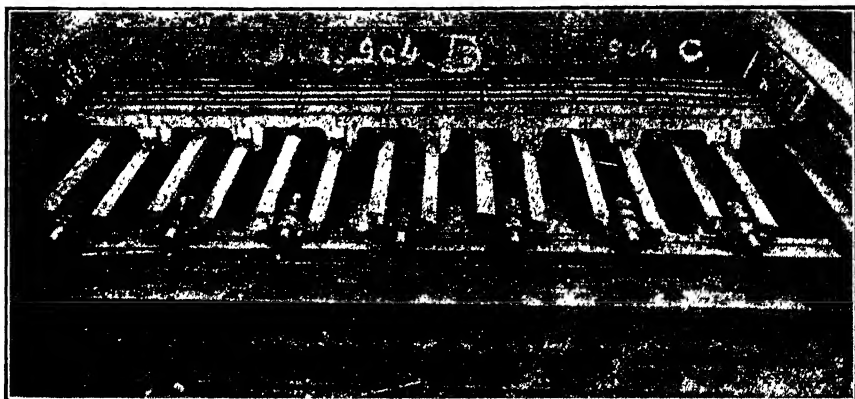

FIG. 8.—AUTOMATIC, SELF-CLEANING GRATE.

Fig. 10 illustrates the method of fluffing the charge while it is being deposited in the sintering pan. The feeding cylinders withdraw the material from the hoppers in layers of definite thickness, which can be easily controlled. At the beginning of the charging, these cylinders are automatically thrown into gear with the charge-car axle, so that the speed
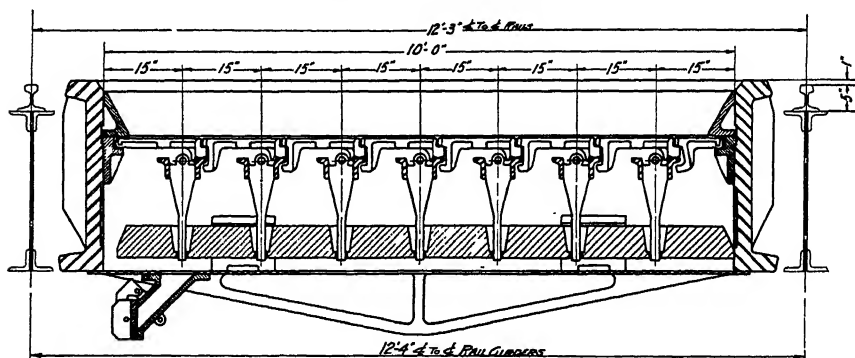
FIG. 9.—METHOD OF MOUNTING GRATE BARS.

with which this layer is withdrawn depends upon the speed of the car. By this means a layer of uniform thickness is deposited in the sintering pan irrespective of the speed of the car. At the end of the pan, the cylindrical feeders are again automatically thrown out of action. The bedding material, if used, consists of a thin layer of coarser material dropped directly upon the grate, but the charge itself is passed over a high-speed fluffing cylinder from which it passes between fingers about

3 in. apart. By intensive fluffing, the thickness of the charge can be increased from 1 to 2 in. owing to increased porosity of the charge.

Fig. 11 is a sectional drawing of the sinter hopper and sinter feeder underneath the pan, and illustrates the method of air-cooling the sinter by passing air through the sinter in the partly filled hopper. The feeder slowly feeds the sinter from the hopper onto the screen, where the fine material is removed for re-treatment. The feeder is sufficiently powerful to crush any large cakes of sinter. When the sintering pan is in a horizontal position, the hopper underneath is sealed, and this brings about the
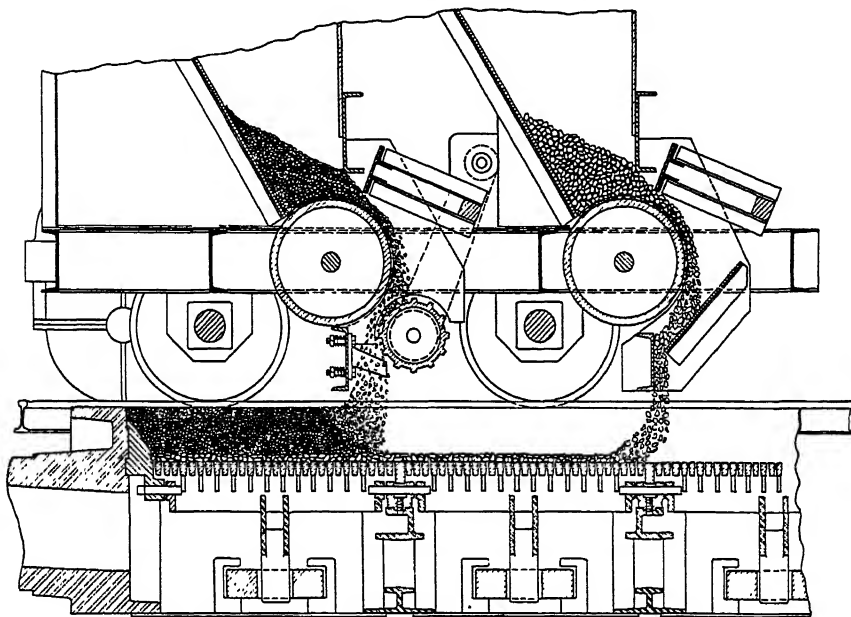
Fig. 10.—Method of fluffing charge.

almost complete elimination of dust from the plant, which is collected in a dust catcher between the hopper and exhauster.

The only limitations to the size of the grate are mechanical, as no difference is noticeable between the results obtained from a small unit and those from a large unit, provided the thickness of the charge, and all other conditions, are the same. The capacity, however, of a unit depends greatly upon the material being sintered. For material such as fine dust and very fine magnetic concentrate, the capacity is from $1\frac{1}{2}$ to 2 tons per square foot of grate area for 24 hr., while for fine ores and granular magnetic concentrate the capacity may vary from 2 to $3\frac{1}{2}$ tons per square foot of grate area. However, the actual capacity must be determined for each material.

Recently we have developed a unit 30 ft. long by 12 ft. wide and 16 in. deep, with an exhaust fan having a capacity of 45,000 cu. ft. of air per

minute at 50-in. water suction.   Four of these units can be operated in series with one set of men.   The normal capacity of each of the units is 900 gross tons of finished sinter per 24 hr.   Such an installation, with its low fuel consumption, would produce sinter at an exceedingly low cost per ton, so that the sintering cost should no longer be an obstacle to its application on a large scale for the sintering of any ore charged into the blast furnace.
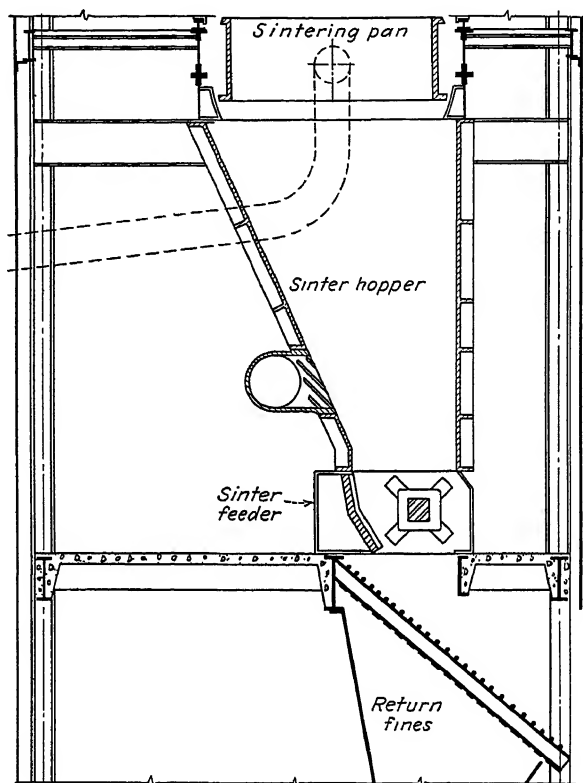

FIG. 11.—METHOD OF AIR-COOLING SINTER.

Some years ago, while inspecting a sintering plant at the works of the Prager Eisen Industrie at Kladno, Czechoslovakia, the writer was informed of the very excellent results obtained with the use of burnt lime in the blast furnace instead of limestone, this bringing about a saving in coke of from 330 to 440 lb. per ton of iron.   This practice is still in use and has been for the last six years or more.   If this reduction in coke consumption can be obtained with burnt lime, it is reasonable to suppose that equally good results can be obtained with a self-fluxing sinter wherein a considerable portion of the lime is already combined with the silica and all of it has been converted from $CaCO_2$ to CaO.   Under these conditions,

we are justified in assuming that even better results can be obtained with regard to coke consumption, and that the capacity of the blast furnace would be increased considerably. According to Avery,[3] the solution loss in the top of the furnace is due to the reaction of CO_2 gas and the carbon of the coke. If there is less CO_2 gas because a sintered flux is used, it seems plausible that the solution loss would be proportionately reduced.

SINTERING OUTSIDE THE UNITED STATES

Sintering of iron ores is progressing faster in Europe than in the United States, because many European ores require beneficiation. Five large plants of the intermittent type are under construction in Europe, and all of these will sinter materials that would not be available for the blast furnace except under adverse conditions. Several of these plants will treat charges composed largely of pyrite cinders. In Italy, there is a scarcity of good iron ore, but very large deposits of iron pyrites. This material is roasted and the sulphur used for the manufacture of sulphuric acid. The residue, or cinders, when carefully sintered to eliminate the sulphur to below 0.10 per cent produces a satisfactory material for the blast furnace.

In the Scunthorpe district in England, the United Steel Companies, Ltd., early in 1935 placed a two-pan plant in operation for sintering the fines from Lincolnshire and Northampton ores. The results with the sinter in the blast furnace were so pronounced that the company immediately started the erection of two more units, and this now is the largest sintering plant in Europe. Two more very large plants are under construction in this district, one intermittent and one continuous.

In Sweden, 15 small sintering plants are in operation as well as a large, very modern, three-pan plant for sintering very fine magnetic concentrate. The Swedish magnetite ores are ground exceedingly fine before concentration, and all of this concentrate is converted into sinter.

USE OF SINTER IN BLAST FURNACES IN THE UNITED STATES

The use of sinter in the blast furnace in the United States has been largely limited to charges in which it played a minor part, therefore the full benefits of the sinter have not been realized. Sufficient work, however, has been done to demonstrate that the pronounced advantages resulting from the use of sinter do not manifest themselves until 50 per cent or more is used in the charge, and the more nearly 100 per cent of the charge is sinter, the better are the results.

One of the early pioneers in this field was the late Tom Kelly, formerly associated with the Witherbee Sherman Co., of Port Henry, N. Y.

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[3] J. Avery: Pressure Operation of the Pig-iron Blast Furnace and the Problem of Solution Loss. This volume, page 102.

TABLE 2.—*Blast-furnace Practice for Month of November 1935, Troy Furnace Corporation*

Day of Month	Iron, Tons	Fuel, Lb. per Ton Pig Iron	Stone, Lb. per Ton Pig Iron	Analysis, Per Cent				Number Stove Heats	Number Top Heats	Blast Pressure, Lb.	Number Charges	Mixture, Per Cent			
				Si	S	P	Mn					Old Bed Sinter	Harmony Sinter	Welland Slag	Sintered Tailings
1	543	1,551	665	1.35	0.021	0.39	0.62	1,180	300	14	79	93.3		1.9	4.8
2	592	1,344	593	1.30	0.021	0.41	0.54	1,150	290	15	78	93.3		1.9	4.8
3	523	1,404	602	1.36	0.022	0.41	0.55	1,200	280	15	70	93.3		1.9	4.8
4	636	1,326	538	1.10	0.022	0.40	0.59	1,260	280	14	76	93.3		1.9	4.8
5	557	1,303	550	1.15	0.020	0.40	0.58	1,210	240	13	68	93.3		1.9	4.8
6	586	1,292	590	1.40	0.020	0.40	0.60	1,130	280	15	77	93.3		1.9	4.8
7	603	1,430	582	1.23	0.019	0.35	0.89	1,150	260	15	78	59.4	31.0	7.9	1.7
8	568	1,264	509	1.10	0.019	0.27	1.87	1,050	260	14	74	65.8	24.3	8.2	1.7
9	567	1,495	621	0.97	0.022	0.30	2.00	1,150	240	15	79	64.9	26.9	9.5	1.8
10	640	1,104	528	0.95	0.020	0.31	1.75	1,160	280	15	75	67.2	21.5	9.5	2.1
11	546	1,461	610	1.00	0.019	0.32	1.93	1,160	260	15	74	72.4	17.9	8.6	2.1
12	546	1,452	691	0.98	0.022	0.31	1.94	1,100	240	14	74	72.6	17.9	8.6	2.1
13	674	1,444	541	0.97	0.021	0.31	1.96	1,150	230	14	81	72.6	17.9	8.6	2.1
14	578	1,382	630	1.10	0.023	0.30	2.00	1,050	200	14	78	72.6	17.9	8.4	0.7
15	564	1,418	622	1.17	0.022	0.31	2.01	1,100	300	15	78	72.7	18.2	8.3	0.7
16	680	1,296	536	0.88	0.023	0.30	2.05	1,200	320	15	81	72.7	18.5	8.4	1.0
17	554	1,470	601	0.87	0.018	0.31	2.00	1,200	190	16	74	72.2	18.0	8.3	1.2
18	561	1,411	609	1.02	0.018	0.30	1.87	1,100	320	18	76	72.8	18.0	8.0	1.2
19	627	1,351	560	0.92	0.019	0.30	1.92	1,150	300	17	78	72.8	13.0	8.0	1.2
20	551	1,555	619	1.00	0.020	0.29	1.79	1,050	320	15	76	72.8	12.5	8.0	1.2
21	516	1,404	636	1.15	0.022	0.30	1.81	1,150	300	15	73	70.1	12.9	8.4	8.2
22	614	1,315	579	1.21	0.021	0.30	1.83	1,000	360	15	79	70.2	12.2	9.6	9.0
23	545	1,447	668	1.35	0.023	0.32	1.85	1,050	380	15	81	70.8	12.9	9.0	8.6
24	609	1,445	597	0.97	0.022	0.32	1.83	1,000	320	15	81	71.1	12.2	9.0	6.7
25	596	1,455	596	1.00	0.023	0.28	1.96	1,000	320	15	79	62.7	26.5	8.4	7.7
26	644	1,322	430	1.00	0.024	0.29	1.90	1,050	380	15	79	65.3	24.2	7.0	2.8
27	617	1,394	576	1.07	0.023	0.28	1.85	1,050	380	15	76	67.3	23.8	6.9	2.3
28	594	1,733	591	1.10	0.022	0.28	1.75	1,050	360	15	78	74.1	17.4	7.2	1.9
29	490	1,666	625	1.10	0.018	0.30	1.80	1,050	320	15	68	91.0		7.2	1.6
30	615	1,301	556	1.15	0.027	0.33	1.83	1,050	330	15	76	90.1		7.1	2.8
Total...........	17,508										2,297				
Average........	583.6	1,395	590	1.12	0.022	0.31	1.59	1,100	290	15	76.5	75.8	14.0	6.9	3.3

Average cubic feet wind per minute.................. 27,000
Coke per charge, lb.............................. 10,500
Total flue dust produced, lb....................... 356,739
Average ore per charge, lb......................... 23,188
Average steam pressure, lb......................... 183

Average per ton pig, lb............................ 20

TABLE 3.—*Blast-furnace Operations for Year* 1936, *Troy Furnace Corporation*

Furnace blown in, May 1, 1936; furnace blown out, Nov. 24, 1936; in blast, 208 days

PRODUCTION

	Gross Tons	Pounds	Lb. per Ton
Foundry..............................	28,524.00	55,334,760[a]	1911
Malleable...........................	10,517.15	20,147,500[a]	1887
Basic.................................	68,338.05	102,632,172	1480
Totals................................	107,379.20	178,114,432	1659
Less coke breeze 1½ in................		2,671,716	
Net coke filled........................		175,442,716	1635

Daily average production, gross tons................... 516
Total flue dirt produced, lb........................... 2,865,688
Flue dust per ton pig iron, lb......................... 26.7
Limestone per ton pig iron, lb......................... 616

TOTAL ALL MATERIALS USED DURING ENTIRE BLAST[b]

				PER CENT
Coke, net tons.................	88,665.12			
Old bed sinter, gross tons........	123,915.45	Fe units.................	67.45	
Harmony sinter, gross tons......	20,635.20	Fe units.................	68.43	
Lean ore sinter, gross tons.......	4,698.55	Fe units.................	12.50	
Lean ore raw, gross tons.........	2,139.50	Fe units.................	12.50	
Hudson Valley ores, gross tons...	3,324.83	Fe units.................	50.00	
Miscellaneous, gross tons........	476.70	Fe units.................	50.00	
	155,190.23			
Manganese slag (W.S.Cp), gross tons.........................	6,043.40	Mn units................	10.00	
Manganese skimmings, gross tons	5,139.78	Mn units................	15 to 30	

166,373.41 ÷ 107,379.2 = 1.549 tons per ton pig
= 64.54 per cent yield

Limestone, net tons............. 33,067.90

PROGRAM

Furnace blown in May 1 on foundry iron to May 10.
Basic, May 11 to July 5.
Malleable, July 5 to July 29.
Foundry iron, July 29 to August 5.
Basic, Aug. 5 to Aug. 25.
Foundry, Aug. 25 to Sept. 24.
Basic, Sept. 24 to Nov. 7.
Pipe iron, Nov. 7 to Nov. 19.
High-silicon foundry, Nov. 19 to Nov. 24, blown out.
Frequent changes as noted above mean higher fuel per ton of pig iron.

[a] Less 1.5 per cent breeze.
[b] During the blast mixtures were changed eight times in order to produce various grades of iron necessary for customers.

TABLE 3.—(*Continued*)
GRADES OF PIG IRON PRODUCED

Silicon, Per Cent		Tons	Per Cent
	1.25 to 1.75............................	8,406	29.5
	1.75 to 2.00............................	1,065	3.7
	2.00 to 2.25............................	2,341	8.2
	2.25 to 2.50............................	3,290	11.5
	2.50 to 2.75............................	5,184	18.2
Foundry	2.75 to 3.00............................	3,665	12.9
	3.00 to 3.25............................	2,455	8.6
	3.25 to 3.50.....	1,175	4.1
	3.50 to 3.75............................	649	2.3
	3.75 and over..........................	294	1.00
		28,524	100.0
	1.25 to 1.75............................	3,097	29.5
	1.75 to 2.00............................	1,080	10.2
	2.00 to 2.25............................	1,562	14.8
	2.25 to 2.50............................	1,459	13.9
Malleable Iron	2.50 to 2.75............................	1,194	11.4
	2.75 to 3.00............................	831	7.9
	3.00 to 3.25............................	830	7.9
	3.25 to 3.50............................	464	4.4
		10,517	100.0

Basic iron, all silicon, 0.75 to 1.35 and manganese 1.50 to 2.50 per cent.

Mr. Kelly was a strong advocate for the use of 100 per cent sinter in the blast furnace, and he repeatedly declared that with such a charge he could make his furnace do everything but talk. He attached great importance to the ease and certainty with which he could produce the exact quality of pig iron desired and the elimination of all "off-iron" casts.

E. L. Keefer, superintendent of the Troy Furnace Corporation, is also a pioneer in the use of high-sinter charges in the blast furnace, and in November 1935 operated the Troy furnace for the entire month with 90 per cent Witherbee Sherman sinter in the charge and with an average coke consumption of 1395 lb. without the use of scrap iron.

The writer is greatly indebted to Mr. Keefer and the Troy Furnace Corporation for the data in Tables 2, 3 and 4 covering the results obtained with this furnace during November 1935 and also the results for the entire year of 1936.

CONCLUSIONS

The writer believes that in the future the sintering plant will attain a position of much greater importance as an adjunct to the blast furnace,

and that before long, all the fines from ores will be converted into self-fluxing sinter. In the still further distant future, he can visualize the sintering of all ores preparatory to treatment in the blast furnace, so that only coke and sinter will be fed into the furnace.

TABLE 4.—*Typical Coke Analysis of Hudson Valley Coke*

Tests	Average, Per Cent	Maximum, Per Cent	Minimum, Per Cent	Number of Tests
Volatile carbonaceous matter	0.9	1.0	0.8	7
Ash	8.5	8.7	8.2	7
Sulphur	0.65	0.67	0.61	7
Phosphorus	0.012	0.013	0.010	7
Shatter test				4
On 2-in. screen	73.9	75.3	71.0	
Tumbler test				4
Stability factor	52.8	54.5	51.8	
Percentage on ½-in. screen	67.2	69.5	63.6	
Hardness factor	68.8	71.4	65.5	
Porosity	47.3			1

The role of prophet is a precarious one, but the prediction can safely be made that the first blast-furnace superintendent to use 100 per cent of self-fluxing sinter properly made, so as to be completely free from iron silicates, will have a most pleasant surprise awaiting him, not only with reference to the greatly reduced coke consumption but also in regard to the increased capacity of the blast furnace and the great uniformity of the furnace operation.

DISCUSSION

(B. M. Stubblefield presiding)

P. G. HARRISON,* Crosby, Minn.—On the first diagram, would it not be possible to eliminate the use of inches of vacuum and substitute therefor units of free air per minute?

J. E. GREENAWALT.—If you get the air through, yes. The advantage of suction is to get air through the charge.

P. G. HARRISON.—Really, the vacuum, as represented in the diagram, is a measure of the inefficiency of the process or the power used; while if the diagram had been made on the basis of free air pulled through the bed per minute, the true measure of the sintering rate would be shown.

J. E. GREENAWALT.—But remember, as I tried to bring out, the porosity of a charge, when once it is on the grate, is definite—the air passages are definite—and in order to get a large amount of air through that charge, you must apply suction.

* Manager, Evergreen Mines Co.

I called attention to the way in which that porosity can be improved.   If you open up porosity, you can decrease suction.

P. G. HARRISON.—In other words, if you get the volume through by increased porosity, you are foolish to go to high vacuum.

J. E. GREENAWALT.—I can get a great deal more air through by higher suction. I can cut down the fuel as a result of strong suction.

P. G. HARRISON.—It burns more rapidly because of more air and not vacuum. It seems to me you have used the thing that costs power rather than the thing that increases capacity, which is air rather than vacuum.

J. E. GREENAWALT.—I am doing something that makes for a successful sintering process with whatever limitations there are at hand.   With a coarse ore, you get the air through freely.   The power itself is not of such vital importance.

I am glad you brought it up, because if you have a porous charge you can get along with much less vacuum, if you want to do it that way.

R. H. SWEETSER,* New York, N. Y. (written discussion).—Mr. Greenawalt's paper brings out some facts contrary to much of the previously published data, which is not surprising when we consider that the sintering of iron ores has as many variations as there are different iron ores and each operator has observed a different set of phenomena.

My first experience with a sintering plant and with the use of sinter were so distasteful that I can appreciate the apparent lag in the general adoption of the sinter plant "as an adjunct to the blast furnace," as Mr. Greenawalt says in his conclusions as to the future of sintering.

There is as much difference between the sinter plants and sinter of the post-war period and the plants and sinter of today as there was between the by-product coke plants and coke of the early Otto Hofman plants and the new coke ovens and byproduct coke of today.   I see such a great similarity between the introduction of by-product coke into blast-furnace practice some 20 years ago and the rather slow adoption of sintered iron ores (outside the almost universal practice of sintering fine magnetic concentrates), that I will approach the discussion of Mr. Greenawalt's paper from a background of blast-furnace and coke-oven experience during the development of by-product coke as the almost universal blast-furnace fuel in this country.

Beginnings.—The beginnings of the making and use of by-product coke for blast-furnace fuel were as crude and nerve-racking as the initial steps in the production and introduction of sintered ores as a major part of the blast-furnace burden.   As in coke, so in sinter, no attention was paid to the hardness, size, porosity, density or moisture contents.   In those days by-product coke was truly the "by-product" of a gas plant or a chemical works, and no consideration was given to the many troubles of the blast-furnace man, who was told that he did not know anything about by-product coke anyway, and must learn how to use whatever the coke-oven man sent him.

Ferrous sinter was at first a necessary evil, and was a beneficiated by-product of the blast furnace itself.   If a bothersome waste product such as flue dust could be returned to the blast furnace as an enriched iron ore it seemed as though it would be an economical thing to use it in large quantities, but, for reasons such as those described by Agnew in his paper,† the furnace could not satisfactorily take larger proportions of sinter in the burden.

The same fallacies that used to prevail among blast-furnace and coke men seemed to prevail in the use of sinter.   One exploded theory, that high ash made a "stronger

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* Consulting Engineer.
† Page 116, this volume.

coke that would carry the burden better," had its counterpart in thinking that a hard, firm sinter was necessary. But Schwartz* recognized the fact that "iron silicates are difficult to reduce"; and, said further, "since we have definitely identified these silicates in practically all samples of sinter examined, and since ordinary iron ore contains only a small amount of iron silicate, it appears that the increased porosity of the charge when using sinter is of such value to the blast furnace that the increase in the percentage of the iron silicate minerals in the sinter is far overshadowed by the increase in porosity. If good sinter could be produced containing no iron silicate this sinter would undoubtedly be better for blast-furnace use."

That this desirable practice in the art of sintering iron ores has already been attained is attested in the papers by Agnew and Greenawalt; one accomplished it by removing the excess silica before sintering and the other by removing the cause for excess temperature and increasing the suction of the air.

I do not agree with Professor Schwartz* in considering that the iron ores "melt." It may be that sinter does, just as the old mill cinder did in the days when we made high-silicon foundry iron. I agree that the mill cinder did have to melt before it could be reduced, but I think that the words "melting of iron ore" are not the correct ones.

It is probable that sinters with high-iron silicate will have to go down low enough in the furnace to be melted before they are reduced, just as was necessary in the old practice of using large percentages of mill cinder in the burden, but that is not a desirable condition. Professor Schwartz suggests that "further work should be done along the line of mixing fluxes with the sintering mixture," and adds that this may help materially in controlling the amount of iron silicate produced.

And this question of porosity, as explained by Mr. Greenawalt, "the porosity of the material to be sintered is one thing and the porosity of the sinter is another thing." Just as in coke and coal, we must have a certain porosity of the coal as it is charged in the coke oven, and we desire to get a certain porosity of coke after it has been quenched.

Porosity is important, particularly with reference to coke. The porosity of the whole blast-furnace burden is a question that has received a great deal of attention lately. The work that has been done in getting a more porous condition of the stock as it is put in the blast furnace has been the beginning of the sizing of ore, coke and limestone. I could not help thinking about it when Mr. Avery was presenting his paper† and speaking of having such high pressures at the top of the furnace. He wanted to double the tonnage. We have done some things in blast-furnace practice that have doubled the capacity of the furnace. Sizing the material and getting the right porosity in coke and sinter will bring about even greater increases in tonnage, I think.

Control of Porosity.—It was an agreeable surprise to me to observe that it is possible to control the porosity and cell structure of iron-ore sinter much in the same way that the porosity and cell structure of by-product coke is controlled. When blast-furnace men went from beehive Connellsville coke to by-product coke it was generally agreed and understood by the furnace men and the coke men that the by-product coke should be hard-burned and in big lumps. But it was different with the blast-furnace men who had been using Pocahontas beehive coke; and they demanded a more open coke, pushed on the "green side."

Today, some furnace men want a porous, fast-burning coke for making basic iron, and a harder over-coked coke for high-silicon iron. Perhaps the question of solution loss, as explained by Mr. Avery, has something to do with this.

Sizing the Sinter.—Just as by-product coke was first used as run-of-oven coke after the coke breeze had been screened out, so has sintered ore been used after the fines

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* Reference of footnote 1.
† This volume, page 102.

have been screened out. The latter have been used as "returns" in the sintering mixture. It has become standard practice to size the by-product coke and to crush the oversize. I believe it will be necessary to size sintered ore in order to get the best results.

C. E. AGNEW,[*] Conshohocken, Pa.—It has been my good fortune to be with the Alan Wood Steel Co. for the past 10 years, during which time we had to work out the problem of using Eastern magnetite ores economically and during this period we sintered Eastern magnetites, domestic and foreign hematites as well as the by-products of other industries.[†]

There is a vast difference in the sintering properties of different materials. The matter of fluffing the charge on the sinter bed is of the utmost importance when sintering soft hematites or any material of an earthy nature. Materials of this nature have a tendency to pack and the packing interferes with the flow of air through the bed, and the burning is uneven. Because of the granular nature of the magnetite concentrates, the tendency to pack is not so pronounced and less trouble of this kind is encountered.

The iron content of an ore is an important factor in the speed with which it can be sintered. For instance, soft hematites that run 50 or 51 per cent iron can be sintered a great deal faster than a magnetite concentrate running 65 to 66 per cent iron.

I have been asked how much sinter we can use. At Alan Wood we have used as high as 97 per cent. I believe the time will come when we will all be using sinter. The proper preparation of the iron-bearing material before it goes into the furnace will eliminate many of the present furnace troubles.

The first action that takes place under the furnace bell is the driving off of moisture, or any carbonate or hydrates that may exist. This work must be done before the material can absorb the necessary heat for reduction to begin. All of this work can be done at the sintering plant.

The sinter fines, if they are sintered, are coarser than the flocculent fines of the soft hematites, and so the use of sinter cuts the flue-dust losses tremendously. At Alan Wood we were blowing at capacity last year and we had a best month of 40 lb. of flue dust per ton of iron. During the month of January 1938, on a 75 per cent blowing schedule, we had 24 lb. of flue dust per ton of iron. For the current month, on 3 per cent silicon foundry iron the flue-dust figure was 38 lb. per ton of iron when I left the plant. These figures are possible because the extreme fines that make flue dust do not exist in a sinter mixture. The carbon in this flue dust has run as high as 19 per cent. This carbon is just coke dust.

The important thing in talking about fuel economy in the operation of a blast furnace is to get the proper contact between the iron-bearing materials and the furnace gas. An ideal stock column would be one in which each cubic foot of material descending through the furnace was identical in its mixture of ore, stone and coke, of equal porosity so that each particle of ore would come into contact with the furnace gas, and of such density that the furnace pressure would be maintained at the maximum point at which the furnace would move itself.

To approach that condition in practice the material must be prepared first. With a soft hematite mixture a certain amount of packing is unavoidable and the furnace gases will find the easiest way through, with the result that some of the ore will work down in the furnace farther in the raw state than it will when using sinter that is properly sized. It has been our experience that sinter of small particle size gives the best results. This can be readily understood because the more compact the stock

column the closer the contact between the ore and gas will be. The smaller the sinter particle size is, without causing excessive furnace pressure, the better the ore-gas contact will be, which means better reduction and lower fuel consumption.

We have also found that we need smaller coke than is used in the Middle West in order to tighten up the stock column and so force the gas contact.

Replying to Mr. Sweetser's question as to the possibilities of increasing the tonnage of a furnace by using sinter, I offer this opinion. The reduction of iron oxide is simply a matter of applying heat units to the iron-bearing material in the presence of a reducing agent. We have used as high as 97 per cent sinter containing approximately 63 to 64 per cent iron. We can run 1500° to 1600° blast temperature on a line; that is our limit. But if we had 2500° of heat, we would have to put on more burden, which would mean more tonnage and lower fuel consumption. Someone is going to design a stove that will give that higher blast temperature, because the sinter will take the heat but the soft ores will not.

A pound of coke of a given carbon content can furnish just so much heat. Every furnace burns the coke completely, but no furnace exhausts the reducing ability of the furnaces gases. This is proved by the CO content of all furnace gas. Additional blast temperature will make the reducing agent more efficient.

P. G. HARRISON.—I received a copy of Mr. Agnew's paper* just before I left home, and it brought some ideas to my mind that are not in accord with his. Possibly in the Middle West they like to have their sinter as coarse as possible because they are using sinters with a mixture of Mesabi ores, which are fine. They want something that will open up the fine-structured Mesabi ores. A different thing is needed for sinter that is to be used as 100 per cent of the burden; a sinter that is fine in structure is needed, so that it will retard the flow of gases rather than accelerate it.

I think that at Alan Wood you had the start toward obtaining a true answer which was never followed out to a logical conclusion. You had had terrible practice with sinter containing 12 per cent silica. Then you screened that sinter into three sizes and found that the practice was improved. As I see it, the screening into three sizes tended to give a blanket in the furnace, which retarded the flow of gases through it, and, therefore, practice improved. Did it ever occur to you to take your sinter and run it off a high trestle onto a plate, so that it would be broken and become all of fine structure? I think that if you would do that you would improve your practice again. Sinter coming down from the Lake Superior country has had that happen to it, because it is the only way of loading an ore boat. I do not think the sinter we make in Minnesota could be put into a blast furnace without previous breaking, because many of the chunks are excessively large. However, by the time the sinter is dropped into a car and then from the car into the ore dock, then into the boat, and is removed from the boat with grabs, the sinter has been considerably reduced. The average screen test of Evergreen sinter taken over a series of years is less than 1 per cent through 100 mesh, and 86 per cent above ⅛ in., with only about 25 per cent in excess of 1 in.; although some of it, when it starts from the mine, is in masses as big as a man's shoulders.

I am going to read some figures from Agnew's paper: "Basic practice—high-silica sinter—Alan Wood Scrub Oak—iron, 59 per cent; silica, 12; alumina, 1; coke, 1950 lb." Of course, that is a very high-yield ore—i.e., 59 per cent iron—and should, on the basis of yield, give an excellent smelting practice. Such yield would be very pleasing to people familiar with ordinary hematites. But suppose we compare this material with a Western washed Mesabi ore that is low in alumina, in the neighbor-

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* Page 116, this volume.

hood of 0.5 per cent. Such an ore is very difficult to reduce in the blast furnace. From various conversations I have had with blast-furnace operators, I gather that it takes at least 2000 lb. of coke to reduce it. In other words, your high-silica sinter and Western washed Mesabi ore concentrates, having a low alumina content, are about equally refractory. There seems here to be no proper answer in the word "fayalite." In both cases there seem to be the results of a very bad alumina-silica ratio.

At Alan Wood the silica in the concentrates was reduced by fine grinding and a high, 67 per cent iron, sinter was made containing only 4.5 per cent silica. In this connection, one should remember that the analyses of a crude magnetite ore and of the sinter made therefrom are approximately the same, while the sinter made from a limonite or hematite is much higher in analysis than the crude ore. With this high-iron low-silica sinter, the coke requirement came down to 1480 pounds.

Now let us take a western washed Mesabi concentrate that runs about 54 per cent iron, 10.50 silica and mix it with an aluminous ore so that the combination of the two is approximately 49.50 iron, 7.50 silica and 2.50 alumina. This mixture can be smelted with between 1700 and 1750 lb. of coke. In other words, allowing for the tremendous difference in yield, we can obtain equally good smelting practice with a properly prepared aluminous ore although it contains 3 per cent more silica and 18 per cent less iron as we can with 67 per cent iron Alan Wood sinter. The alumina ratio, therefore, seems to be more important than the condition of the silica in a particular ore or sinter.

Suppose we go clear back. These figures are so far back that I am not certain that they are correct. Let us remember the old eastern blast-furnace practice in which crude magnetite analyzing 60 per cent iron and 12 per cent silica was charged—the analysis of this crude magnetite being approximately the same as the high-silica sinter made at Alan Wood. With this charge the gas was simply blown through the furnace, and it required anywhere from 2600 to 3400 lb. of coke to make a ton of iron. The structure of the charge was terribly open, with the result that the heat was being blown out through the top of the furnace, somewhat as happened with the high-silica sinter, as is indicated by the high top heat with this material. It was later found out that smelting practice on magnetite could be substantially improved by crushing. A still greater improvement was occasioned by crushing and grinding of the magnetite and transforming it into sinter. This conversion changed a substantial portion of the silica in the magnetite into fayalite. Despite this change of silica into fayalite, the smelting practice was improved by several hundred pounds of coke per ton of iron. This improvement was evidently the result of improved structure and lowered silica; certainly not because part of the silica in the ore in the form of quartz was changed in the sinter to the form of fayalite.

Suppose we again go to Alan Wood and take their foundry practice. I have been referring to their basic practice. Using high-silica sinter and making 3 per cent silicon iron, they used 2450 lb. of coke; after improving their concentrating practice and making a low-silica sinter, they reduced the coke required to make a ton of pig iron to 2000 pounds.

Suppose we now compare this practice with a Lake front furnace using high-silica sinter and Lake Superior ores. At one Lake front furnace, the standard burden is 30 per cent of sinter running from 10.00 to 11.00 silica and 4.50 alumina, 50 per cent Menominee ore, 7 per cent siliceous and 13 per cent Mesabi, with a resultant practice of 1700 lb. of coke per ton of iron or 300 lb. better than obtained at Alan Wood. The difference in yield here again is very great; the Lake front furnace having about 51.50 per cent of iron in the burden as against 67 per cent in the Alan Wood sinter. The Alan Wood sinter should certainly give a better smelting practice than 2000 lb. unless there is something in the slag-forming and reducing qualities of the burden. The essential difference is, I believe, in the silica-alumina ratio, which is held at the Lake front furnace to about 17.50 per cent of alumina in the slag.

At another Lake front furnace we have record of the burden being 49.93 iron, 12.49 silica and a small amount of scrap. This furnace obtained a coke figure of around 1600 lb. Allowing for the melting of scrap at 700 lb. of coke per ton of scrap melted, the comparable figure is approximately 1700 lb. of coke per ton of pig iron made from the ore. Again a practice of approximately 300 lb. of coke per ton of pig iron better than that obtained at Alan Wood.

In other words, from data I have hurriedly assembled and without detailed compilation from many other sources, it seems to me that the real answer to the problem is that you simply eliminated silica and by such elimination obtained the results normally to be expected therefrom. It costs money to melt silica. Some years ago, I attended a meeting at which the question came up: "How much does it cost to smelt silica, in excess of the amount you need for slag?" The figures given varied all the way from 5¢ to 30¢. Suppose we take 15¢ as the cost of removing silica—on the basis of $5 coke this would be 60 lb. of coke per unit of excess silica. In the Alan Wood practice, dropping from high-silica sinter at 12.00 per cent to low-silica sinter at 4.50 per cent, there would be an expected saving of $7\frac{1}{2} \times 60$, or 450 lb. coke, simply because excess silica was removed, and not because there was any change in the silica from fayalite to nonfayalite. The remarkable improvement obtained at Alan Wood was simply the result of eliminating excess silica, which was not balanced by a proper smelting proportion of alumina.

C. E. AGNEW.—In answer to the question of fayalite. In this particular ore from Scrub Oaks mine that gave us so much trouble, apparently the alumina and iron were combined and the silica free, so that when we had a 12 per cent silica concentrate the alumina was 1.25 per cent, but as we reduced the silica the alumina was raised to 2.5 per cent, and we had a much better balance.

The silicate, which was largely in the form of fayalite, formed when sintering the siliceous concentrate. The sinter was large and lumpy. The large lumps would retain their size even though handled and dropped several times.

Our first move was to size the sinter by screening as was done with the ore at Provo, Utah. This was when we still had some hematite in the sinter mix. We thought we had the problem solved but when we got to a straight magnetite mix we found we had not. Even after screening and crushing the oversize we still could not get good furnace practice. I just cannot agree with you that fayalite is not the answer.

P. G. HARRISON.—It seems to me that this gives me exactly the answer I want. If your sinter has been excessively hard as the result of high silica, you have had bad smelting practice because you were practically charging lump magnetite into your furnace; it was the structure of the sinter that was detrimental, and not the chemistry.

When a silicate is formed in a sinter from a hematite containing considerable alumina it is not a true fayalite but is a silicate having a much lower melting point; therefore, irrespective of the sintering practice, you do not get the same smelting results from the melting of silicates formed in sinter from ores containing high alumina, nor for that matter, from ores containing high magnesia, lime, or other basis, which result in a lower melting point than true fayalite, which can only be formed from ores that are practically void of these elements; i.e., magnetite.

C. E. AGNEW.—I will say again on that subject, in our particular ore we are unfortunate in having no other elements to act as a base. Softer hematites will sinter more easily and give a better balance of elements, and calcium or aluminum silicate possibly is formed before an iron silicate, and it does not hurt the practice a particle. In years past we sintered the same high-silica concentrate with about 50 per cent of soft hematites and obtained good results, but not nearly as good as we are getting now.

There is no mystery about what we are doing.   We have a high-iron mixture that reduces easily, and we are able to run high heats.   I am running 1500° to 1600°.   The material will take that heat whereas soft hematites will not.

B. M. STUBBLEFIELD,* Youngstown, Ohio.—I suppose a good chairman should remain neutral, but there is one thing in this discussion that interests me.   Mr. Greenawalt brought out in his illustrations that in these sinters there is really iron oxide surrounded by a wall of so-called glass, as he termed it.   You are talking about the ratio of alumina to silica, and Mr. Greenawalt mentioned the fact that he wants to produce a self-fluxing sinter.   It is therefore my opinion that the sinters under discussion are hard to reduce because the glass must be melted from the particle of oxide before the furnace gases can react with it, not because the sinter contains fayalite.   Mr. Greenawalt's suggestion of adding a flux should help, as the addition of alkalies should reduce the melting point of the silicates and thus free the oxides of their glass coating higher up in a furnace.

H. J. STEHLI,† New York N. Y.—A point has been brought up that is very important.   The effect of fayalite is this: it acts as a varnish or coating over the particles of iron oxide in whatever form they may be.   As the sinter goes down in the furnace, if there is such a coating reduction does not begin until a zone is reached where the temperature is above, say, 1500° C., which is the melting point of fayalite.   If there is a coating composed of silica, iron or calcium silicate, which has a melting point of around 1050° C., there is an earlier melting of that coating and a freeing of the oxide particles, so that the gases can work on them much higher up in the column than when the coating is the high-melting-point fayalite.   That is the main thing about this so-called glass.

I should like to touch on the effect of sinter on the blast furnace.   In the early days, sintering was used entirely on lead blast-furnace charges.   Before sintering was adopted, a lead blast furnace used to do 1½ or perhaps 2 tons of charge per square foot of hearth area in 24 hr.   When sintering was first used, it was applied only to fine sulphide ores, which it was necessary to sinter.   But it was soon found that there were definite benefits to be obtained from the better physical character of sinter in the charge and that the furnace practice improved, and more and more of this furnace material was sintered.   Today, in lead blast-furnace practice, many of the by-products, such as fume, are put over the sintering machines because of the greatly improved physical condition in the sintered form.   The result is that the lead blast furnace of the same construction that some years ago smelted only 1½ or 2 tons per square foot of hearth area now handles 8 tons, and where formerly 13, 14 and 15 per cent coke was used on the charge, today only 10 per cent is used, or around that amount.   So it has very definitely been proved in lead-furnace practice that there is a very definite advantage in sintering the entire charge.   Today, when anything goes wrong, the operators do not look around the furnace; they go straight to the sintering plant to see what kind of sinter is being produced.

R. W. HYDE,‡ New York, N. Y.—So far as sintering itself is concerned, there is theoretically no difference between a continuous and an intermittent operation.   The difference is that one is a continuous operation of proportioning the charge, mixing and carrying it through the sintering step, while the other is a batch process throughout.   If preparation could be as good in one case as in the other, equally good results should be obtained.

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* Youngstown Sheet and Tube Co.

† Sintering Machinery Corporation.

‡ Metallurgist, Dwight and Lloyd Companies.

I was particularly interested in what Mr. Greenawalt said about the time and temperature factors affecting the formation of silicates. We all know that time is just as important as temperature in chemical operation—which is what sintering is. And if you can conduct your sintering operation at a rapid rate, although you may reach a temperature where fayalite could form in time, if you don't give it time enough you will not form any fayalite. Mr. Greenawalt's photographs of sinter high in silica but free from fayalite bring this out very clearly. In the old days, when flue dust with 15 to 30 per cent carbon was sintered, very high temperatures were reached and were held for some time while the 10 to 25 per cent excess of fuel was being burned out. Under these conditions silicates would probably be formed, and this no doubt accounts for the prejudice that some blast-furnace operators had against sinter. The fact that such flue dust had enough excess fuel to serve for sintering several times its own weight of fine ore, and that mixing fine ore with it would give a better product and an all-around economy, was preached for years before the operators could be made to adopt the practice.

H. J. STEHLI.—I think the sintering plant has been looked upon by a great many furnace men as a troublesome thing, the only excuse for having it being to eliminate the blast-furnace flue dust. Looked at in that light, it is a necessary evil. It ought to be looked upon as a real means of improving the character of the charge, and if it is given a little attention it will make a big difference. If you can study your charge and the operation of the plant, and make a good sinter product, you will find a decided advantage.

B. M. STUBBLEFIELD.—How much did this beneficiation increase the lead content of the ore?

H. J. STEHLI.—Well, it did not increase the lead content very much. There was a shrinkage of weight in sintering, perhaps 10 or 15 per cent, depending upon the constituent of the charge. In sintering carbonate iron ores there is a greater weight shrinkage than with the iron in the form of magnetite. But that would be a fair average, 10 or 15 per cent shrinkage, and the lead content was increased proportionately.

C. HART, Media, Pa.—Of course, we are talking about increasing 20 or 25 per cent iron content in the ore. As I understand it, the increase in the lead content of your lead furnace would not be in excess of 10 per cent.

H. J. STEHLI.—Not the increase of the lead content; the charge was not over 10 per cent.

C. HART.—So there is more benefit in the lead furnace in the conditioning of the lead charge than in the blast furnace.

H. J. STEHLI.—There is a big advantage in the conditioning of the charge; in fact, it has been called predigested food for the blast furnace, because the blast furnace did not have much to do except the small amount of reduction in the smelting.

Efficiency of the Blast-furnace Process

By J. B. Austin*

(New York Meeting, February, 1938)

IN considering so complex a process as the smelting of iron in the blast furnace, there is obviously no single method of calculating efficiency that gives a complete appraisal of the performance of the furnace in all its several functions; such a comprehensive view as is required to evaluate producing ability and manufacturing costs for a given furnace is obtained only by considering a group of efficiencies, each of which measures the performance of the furnace from a specific point of view. For instance, there is the rate of consumption of coke per ton of iron produced, which is probably the most frequently considered, and is certainly one of the most important of the group; there is the efficiency of recovery of iron charged; and there is the efficiency of utilization of energy, both chemical and thermal, in some respects related to the former two yet in other ways independent of either. In each of these cases, the calculation can be made on the basis of the actual input of material or energy, or it may be based upon a comparison with the minimum amount of material or energy that would be required by a "perfect" furnace; that is, an imaginary ideal furnace analogous to the perfect steam engine used in thermodynamic calculations, when this furnace is operating under optimum conditions. Moreover, the furnace itself can be considered either as an apparatus for smelting iron or, taking a somewhat less common point of view, as a gas producer yielding iron and slag as by-products. Some of these efficiencies are more useful than others, yet all are instructive; for a knowledge of them not only leads to good engineering practice from the standpoint of control but also discloses limits to possible improvement in performance and indicates the lines along which improvement is most likely to be profitable. Estimates of some of these efficiencies have appeared from time to time in the literature, but many of them are open to objection because they are based on data of uncertain accuracy or because they have been calculated without due regard to the thermodynamic principles involved. Moreover, so far as the author is aware, no general survey of the blast furnace comparing its performance in all the aspects mentioned has been made.

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* Research Laboratory, United States Steel Corporation, Kearny, N. J.

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It is the purpose of this paper to consider and to compare these several efficiencies as calculated from the most reliable data now available. Clearly, a complete and detailed study of such a broad subject can scarcely be contained in anything smaller than a book, so that no attempt is made to supply detailed calculations in every instance; the aim is rather to present a point of view, chiefly as regards the performance of a perfect furnace, with only occasional resort to numerical values, leaving detailed calculations to be carried out by the reader for the cases in which he may be interested. The discussion contains little that is new, most of it having been given before by others, though usually in somewhat different form, but repetition is justified by the fact that misunderstanding of the fundamental role played by chemical and thermal equilibria in the smelting process continues to exist. The author, realizing that many limitations of practical operation have been neglected, wishes to emphasize that this discussion is not intended to be a manual for operating a furnace, but seeks to derive from established chemical and physical principles some idea of the performance achieved by a perfect furnace; in other words, an attempt is made to set up a par value or bogy with reference to which the performance of a real furnace can be compared.

But before evaluating the blast furnace in terms of perfect performance, it is interesting to see how the efficiency of this furnace, which uses coke both as fuel and as source of reducing agent, compares with that of other possible processes in which a different method of heating or a different reducing agent is used. This can be done conveniently by considering the principal functions of an iron smelter, which are: (1) drying and preheating the charge; (2) calcination of carbonates and fluxing of gangue materials; (3) reduction of metallic oxides in the ore; (4) melting and superheating the iron and slag produced.

Three of these items—namely, preheating, fluxing and melting—are essentially heating operations for which the heat requirement is essentially the same in all processes producing pig iron, since the heat that must be supplied is fixed by the nature of the charge and the grade of iron being produced, and is independent of the method of heating used. The same is true of the important factor of the temperature attained in the hearth, since this is also determined by the grade of iron produced and is independent of the method of supplying the heat. Consequently, as far as these operations go, all methods capable of supplying the necessary amount of heat and the required temperature are in principle equivalent. Any advantage of one over the other that appears in practice is due to an advantage gained in the design of equipment or to an economic factor such as a much lower cost of one form of heating in a given locality. Inasmuch as the blast furnace, using coke as fuel, produces both the amount of heat and the temperature required, and conserves each throughout the process with relatively small loss, it satisfies the require-

ment and is therefore in principle as efficient thermally as any other method. From an economic standpoint it is superior to other methods in locations where metallurgical coke is produced in sufficient quantity at a relatively low cost.

The situation is somewhat different with the fourth function, the chemical operation of reducing metallic oxides, because here the amount of heat required differs widely with different reducing agents. This is illustrated by the data in Table 1, which give for two temperatures the

TABLE 1.—*Heat Absorbed (Positive) or Evolved (Negative) in Reducing One Pound of Iron from Fe_2O_3 by Means of Different Reducing Agents*

Reaction	Heat Effect, B.t.u. per Pound Fe	
	At 70° F.	At 1650° F.
$Fe_2O_3 + 3H_2 = 2Fe + 3H_2O$	502	134
$Fe_2O_3 + 3C = 2Fe + 3CO$	2,334	2,076
$Fe_2O_3 + 3CO = 2Fe + 3CO_2$	−92	−339

heat absorbed (positive) or evolved (negative) in the reduction of 1 lb. of iron from Fe_2O_3 by hydrogen, by carbon, and by carbon monoxide, the only reducing agents likely to be commercially feasible. With hydrogen there is a small absorption of heat, with carbon a large absorption, but with carbon monoxide the reaction is exothermic and there is a small evolution of heat. From a purely thermochemical standpoint, therefore, reduction by means of carbon monoxide, which results in a slight gain in heat, is better than reduction by either carbon or hydrogen, in which heat must be supplied to keep the reaction going. On this same basis, reduction with carbon monoxide itself is obviously better than with a mixture of carbon monoxide and hydrogen.

Summing up over all the operations carried out in smelting iron, it is clear that reduction with carbon monoxide as carried out in the blast furnace is in principle much the most efficient way of producing pig iron. This superiority becomes even more marked when one considers that in the blast furnace the coke produces heat and high temperature at the place where they are most valuable, that is, in the hearth, and at the same time supplies carbon monoxide, which is the most efficient reducing agent. The blast furnace, therefore, is much more efficient thermally than a process in which the reduction is carried out by carbon monoxide with some source of heat other than burning coke, and this in turn is better than a process using carbon or hydrogen as the reducing agent. Indeed, the high efficiency of the blast furnace compared to other iron-smelting processes that have been proposed from time to time is due to the very efficient way in which the carbon and carbon monoxide are used.

Material Efficiency of the Smelting Process

Recovery of Iron

Considering the blast furnace as a smelter, the first efficiency to be considered is the recovery of the iron charged. In all modern furnaces more than 90 per cent of the iron in the charge is recovered directly as pig iron, a yield that is remarkably good for a single operation, there being relatively few chemical reactions carried out on a large scale that can approach it. In fact, it would often be considered a satisfactory recovery for a process that includes the working of waste materials. The only metal losses are in slag and in flue dust, and as the latter is usually returned to the furnace as dust or as sinter the net efficiency may, and often does, exceed 95 per cent.

Consumption of Carbon

Turning to the question of coke consumption there is an immediate difficulty in selecting a proper basis on which to calculate the efficiency, because coke serves as both fuel and chemical reagent; that is, it not only supplies heat but is the reducing agent as well. As the demands of both these uses must be met, it is logical to select as a basis the one that requires more carbon, because this is the use that in actual operation fixes the amount of coke consumed. The problem becomes, then, one of determining, or at least approximating, the amount of carbon required as fuel on the one hand and as reagent on the other.

A calculation of the amount of coke required as fuel is not a simple matter; indeed, it is not even a definite problem because combustion of coke is not the only source of heat in the furnace. An appreciable fraction of the total heat is brought in by the hot blast, which, incidentally, is one of the means commonly employed to regulate the heat supply. Nor is the total amount of heat required the only consideration. Other factors that must be taken into account are: (1) the place where the heat is supplied, since economical operation depends upon a proper balance between the heat generated in the hearth zone and that required in the hearth as well as in the reducing zone; and (2) the temperature at which the heat is delivered, because this heat, to be effective, must be furnished at, or above, some minimum temperature, which is largely determined by the grade of iron being produced. It appears therefore somewhat simpler to calculate the minimum amount of coke required for reduction and then to see whether the heat generated by this coke in combustion, plus the heat that can be conveniently brought in by the hot blast, is sufficient to supply the requirements of the furnace.

Carbon as a Source of Reducing Gas

Considering carbon as a chemical reagent, it is possible to base an efficiency for the over-all reduction of iron from Fe_2O_3 on the stoichiometric relations expressed in the equations

$$Fe_2O_3 + 3C = 2Fe + 3CO \qquad [1]$$
$$Fe_2O_3 + 3CO = 2Fe + 3CO_2 \qquad [2]$$
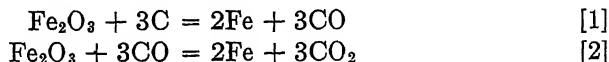
which show that 720 lb. of carbon, either as coke or as carbon monoxide, react with 3210 lb. of Fe_2O_3 to give 2240 lb. of iron. Thus, the efficiency can be defined as the ratio of this amount of carbon to that required in an actual furnace. But such a procedure is misleading because it implies a possibility that a ton of iron can be obtained in practice with an expenditure of only 720 lb. of carbon, which is not true except under very special circumstances. It can be done if all the reduction is "direct;" that is, if it is carried out by direct reaction between carbon and the iron oxide, so that the carbon monoxide formed escapes—as, for instance by letting an oxide slag react with a bath of molten iron saturated with carbon.*

But it cannot be done in a blast furnace or any other apparatus in which all, or nearly all, of the reduction is carried out by means of carbon monoxide, because equilibrium conditions make it necessary to maintain a considerable excess of carbon monoxide in order to keep the reaction going in the desired direction and to prevent its reversal, which would mean reoxidation of iron by the carbon dioxide formed. Any conclusion drawn from the calculation of such an efficiency is therefore erroneous when applied to blast-furnace reactions, in precisely the same way that the efficiency of a steam engine would be wrongly stated if calculated without regard to the theoretical efficiency of the cycle on which the engine operates. A more accurate evaluation of performance, for the blast furnace as well as for the steam engine, is obtained by calculating a relative efficiency based on the performance of some furnace, or engine, which operates in such a way that it achieves the maximum utilization of energy, chemical or thermal, permitted by the second law of thermodynamics. For the steam engine, the Carnot cycle provides such a standard efficiency, but no corresponding measure has as yet been established for the blast furnace, although an approximate one—which is in essence identical with the Carnot cycle—can be set up, as is shown below.

The development of this standard is most easily understood by starting with a consideration of equilibrium in the reaction between ferrous oxide and carbon monoxide, which, in so far as coke consumption is concerned, appears to be the most important reaction occurring in the blast furnace, because of the large amount of carbon required to carry

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* The reader is reminded that in this paragraph only carbon required as reagent is considered, heat requirements being neglected for the moment.

out this last step in the ore reduction. The so-called equation for this reaction, that is,

$$FeO + CO = CO_2 + Fe \qquad [3]$$
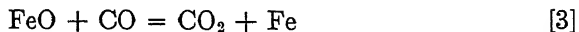
is nothing more than a statement in chemical shorthand that whenever one formula weight of ferrous oxide is reduced one formula weight of carbon monoxide disappears and one formula weight of carbon dioxide and one of iron appear. Or it may with equal validity be applied to the oxidation of iron by carbon dioxide, for which it states that when one formula weight of carbon dioxide reacts with a formula weight of iron, one formula weight of carbon monoxide and one of ferrous oxide are formed. In other words, it is in effect a specialized statement of the law of conservation of matter, and is analogous to the law of conservation of energy.

The equation does not imply that all mixtures of carbon monoxide and carbon dioxide will reduce ferrous oxide, any more than it implies that all such mixtures will oxidize iron. In fact, it tells nothing whatever as to which mixtures are oxidizing or reducing in relation to either iron or ferrous oxide. Moreover, it makes no mention of temperature, yet there is a whole range of mixtures of carbon monoxide and carbon dioxide that will be reducing at one temperature and oxidizing at another. In order to predict the behavior of a given mixture, it is necessary to know the equilibrium mixture for the reaction at the temperature in question, and this can only be determined by direct experiment or by thermodynamic calculation if the necessary thermal data for the several substances involved in the reaction were available. If at a particular temperature a given mixture contains a higher concentration of carbon monoxide than the equilibrium mixture at that temperature, the mixture will tend to reduce ferrous oxide and not to oxidize iron; conversely, if it contains more carbon dioxide than the equilibrium mixture, it will tend to oxidize iron but will not reduce ferrous oxide.

Direct measurements of the equilibrium in this reaction show that at the temperatures prevailing in the lower part of the blast-furnace stock column only about one-third of the total carbon monoxide is available for reduction. To take a specific example, if a limited volume of pure carbon monoxide is brought into contact with a mixture of ferrous oxide and iron at 1650° F. (900° C.) reduction of ferrous oxide proceeds, rapidly at first but at a decreasing rate as carbon dioxide accumulates in the gas, until the gas has attained a composition of 68 per cent carbon monoxide and 32 per cent carbon dioxide, when reaction ceases. If we start with a limited volume of pure carbon dioxide there is oxidation of iron, again at a decreasing rate, with cessation of reaction when 68 per cent of the carbon dioxide has been converted to carbon monoxide. This mixture of 68 per cent carbon monoxide and 32 per cent carbon dioxide is therefore in equilibrium with ferrous oxide and iron at 1650° F. (900° C.)

and represents the maximum possible utilization of carbon monoxide in the reduction of ferrous oxide at that temperature. The residual carbon monoxide is unavailable in this reaction in precisely the same way as the units of sensible heat in a mass of gas at 1650° F. (900° C.) are unavailable for heating anything above 1650° F. (900° C.), no matter how many of them there may be. In other words, equilibrium in this chemical reaction limits the extent to which we can utilize chemical energy just as the second law of thermodynamics limits the extent to which we can utilize thermal energy. As a consequence, 68 per cent of the carbon monoxide heated to 1650° F. (900° C.) remains unutilized in the reduction of ferrous oxide at that temperature; so that to utilize 32 per cent of our carbon monoxide we must heat 100 per cent, or over three times as much ($^{10}\!\%_{2}$ = 3.1). A more appropriate picture of conditions at this temperature is therefore given if we write the equation

$$FeO + 3.1CO = Fe + CO_2 + 2.1CO, \text{ at } 1650° F. (900° C.) \quad [4]$$
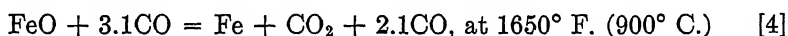
Experiment also shows that there is an equilibrium mixture of carbon monoxide and carbon dioxide characteristic of the reduction of each of the three oxides of iron, that is, the reduction of Fe_2O_3 to Fe_3O_4, of Fe_3O_4 to FeO and of FeO to Fe, and that each of these equilibria varies with temperature. The equilibrium composition of the gas over each pair of solid reagents, as listed above, and at any temperature can therefore be represented by the diagram shown in Fig. 1, in which the solid lines give the result of direct measurements. This diagram tells us that in order to produce iron and to keep it from being reoxidized, the final concentration of carbon monoxide in the gas must at a given temperature be greater than the equilibrium concentration shown for that temperature by the line AB. The minimum amount of carbon as CO required to produce a ton of iron is, therefore, that consumed in the actual reaction, as given by equation 3, plus that amount required to maintain the necessary excess of CO as indicated by Fig. 1; in other words, at each temperature it is given by an equation similar to eq. 4 for 900° C. This result applied to an imaginary perfect furnace, working under equilibrium conditions throughout—that is, at equilibrium in the reduction and with perfect countercurrent operation in the rest of the process—enables us to set up a

Fig. 1.—Equilibrium concentration of CO in reduction of iron oxides (full lines) and in solution reaction (dashed line).

standard for the performance of an actual furnace, corresponding precisely to the Carnot cycle as the standard for the performance of a steam engine.

Let us imagine such a furnace as consisting of three chambers with connections for passing gas from one to another. In the first chamber Fe_2O_3 is reduced to Fe_3O_4, in the second Fe_3O_4 is reduced to FeO and in the third FeO is reduced to Fe. It is assumed that at the start each chamber contains enough oxide to yield a ton of iron, that all three chambers are at the same temperature, that the reducing gas contains only CO and CO_2, that all reduction is indirect—that is, effected by means of CO—and that there is no loss of material as flue dust. The restriction that the reducing gas contain only CO and CO_2 is entirely a matter of convenience because the presence of an inert gas such as nitrogen merely dilutes the active gases but does not change their ratio, which is the governing factor. The operation of such a furnace corresponds very closely with the ideal operation of Grüner in that all the reduction is indirect. It should also be emphasized that this perfect furnace in which the reduction takes place in steps is not intended to be a counterpart of an actual furnace, any more than the thermodynamic engine used to demonstrate the operation of a Carnot cycle need be a counterpart of a steam engine, but it is used because it permits us to carry out the reduction with carbon monoxide at maximum efficiency.

As the equilibrium concentration, hence the carbon consumption, varies with the temperature at which the perfect furnace operates, it is of interest to calculate the carbon required per ton of iron produced for several different temperatures, to learn the magnitude of the variation. Taking first the relatively low temperature of 1500° F. (815° C.), we shall consider the operation of the perfect furnace in detail, starting with the chamber in which FeO is reduced to iron because this step (Fig. 1) requires the highest $CO:CO_2$ ratio. The line AB in Fig. 1 shows that at this temperature only 36 per cent of the CO is effective for reduction, consequently there must be a total of $^{100}/_{36}$ or 2.8 mols of CO and the process can be described by the equation:

$$FeO + 2.8CO = CO_2 + Fe + 1.8CO, \text{ for } 1500° \text{ F. } (815° \text{ C.})$$
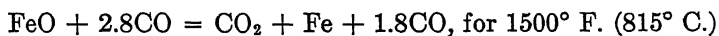
Thus, if we start with 2880 lb. of FeO, enough to give 2240 lb. of iron, a minimum of 1343 lb. of carbon is required, of which 480 lb. is for actual reaction and 863 lb. goes to maintain the indispensable excess of CO. Allowing for coke with 90 per cent fixed carbon, this represents a coke consumption of 1498 lb. per ton of iron, as the minimum necessary to furnish the chemical reagent or the amount required under perfect conditions at this temperature.

After the production of a ton of iron, the residual gas is transferred into the next chamber, which contains enough Fe_3O_4 to supply 2880 lb. of

FeO. This residual gas contains 64 per cent CO, an amount that is considerably in excess of the equilibrium concentration of 28 per cent CO (curve AE, Fig. 1) for this pair of oxides at the same temperature of 1500° F. (850° C.); consequently the gas can reduce Fe_3O_4 and continues to be reducing as long as the concentration of CO remains above that at equilibrium. As the amount of carbon required for actual reaction in reducing Fe_3O_4 to FeO is only 159 lb. per ton of iron, and as the residual gas contains 863 lb. of carbon as carbon monoxide, the gas can supply all the carbon necessary for reduction without having the CO content fall below 52 per cent, which is nearly twice the equilibrium concentration, at which reaction would cease.

After complete reduction of the Fe_3O_4 to FeO, the residual gas is transferred to the first chamber which contains Fe_2O_3. As the gas at this stage contains 52 per cent carbon monoxide, which is many times the equilibrium concentration of CO in contact with Fe_2O_3 and Fe_3O_4, it reduces Fe_2O_3, and since it contains 704 lb. of carbon as carbon monoxide, it can supply the 80 lb. of carbon required for reduction without appreciably changing the $CO:CO_2$ ratio. It is evident therefore that a gas that contains enough carbon monoxide to reduce 2880 lb. of FeO to give 2240 lb. of iron under equilibrium conditions at this temperature contains more than enough CO to reduce an equivalent amount of Fe_3O_4 to FeO and of Fe_2O_3 to Fe_3O_4 as well.

It should be noted that the total carbon required for actual reaction with oxides of iron in order to produce a ton of iron from Fe_2O_3 is 480 lb. for reduction of FeO to Fe + 160 lb. for reduction of Fe_3O_4 to FeO + 80 lb. for reduction of Fe_2O_3 to Fe_3O_4, or a total of 720 lb., which is just what was calculated from equations 1 and 2, whereas a minimum of 1343 lb. of carbon is needed at this temperature for the reactions described, which represent the most effective utilization possible of carbon in reduction of iron oxides to iron with CO. The difference of 623 lb. represents the excess carbon as carbon monoxide that is necessary to maintain a reducing atmosphere but is rejected at the end of the process. In practice this excess must be even greater than 623 lb. because it is necessary to have more CO than is required at equilibrium in order to have an appreciable rate of reduction.

Similar calculations at other temperatures show that throughout the temperature ranges likely to be found in the stock column the amount of carbon necessary to meet the equilibrium requirements in the reaction between ferrous oxide and carbon monoxide is also sufficient to carry out the earlier steps, the reduction of Fe_2O_3 to FeO. It is therefore not necessary to consider further the earlier steps and we may focus attention on the carbon requirement of the final step; that is, the production of metallic iron from FeO. Furthermore, this relation will, in general, hold for an actual blast furnace even though the reduction does not actually

take place at a single temperature, so that we can with some confidence apply the conclusions drawn from the operation of the perfect furnace to an actual furnace, without making any assumptions as to reduction in definite steps at definite temperature levels.

At a higher temperature—for example, 1800° F. (980° C.)—the equilibrium requirement for the reaction $FeO + CO = Fe + CO_2$ is somewhat less favorable and more carbon is required. A calculation similar to that just made shows that at this temperature the minimum requirement is 1636 lb. of carbon, or 1840 lb. of coke, on the basis that the coke contains 90 per cent fixed carbon. Calculations for other tempera-
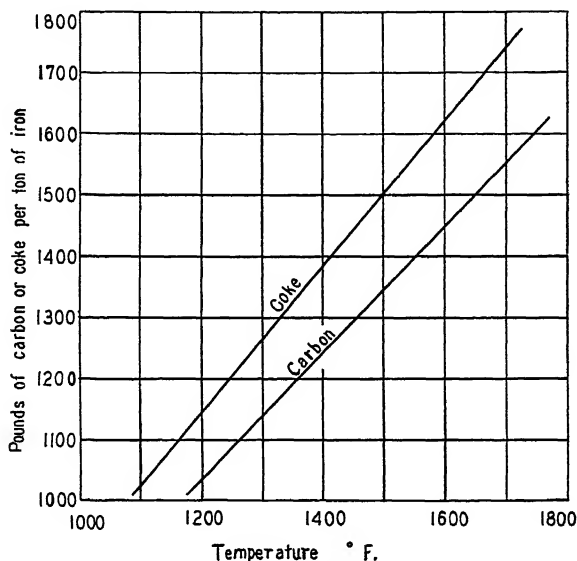
FIG. 2.—TEMPERATURE VARIATION OF AMOUNT OF COKE AND CARBON REQUIRED BY IMAGINARY PERFECT BLAST FURNACE WORKING UNDER OPTIMUM CONDITIONS.

tures lead to the data shown by curves 1 and 2 in Fig. 2; curve 1 giving the minimum amount of carbon required, curve 2 the corresponding amount of coke. It is assumed in each case, of course, that all the reduction is carried out by means of CO; consequently, these values correspond to the coke consumption under ideal operation as postulated by Grüner.

If, however, the operation of a furnace should be such that reduction is not complete in the stack and some appreciable amount occurs in the hearth zone by direct reaction between iron oxide and carbon, the coke consumption calculated to meet the requirements of the reducing reaction as to chemical reagents (i.e., not considering thermal requirements) might be lowered slightly below the values given in the figure. (A condition of this kind might result if the charge contains iron-bearing materials that for one reason or another, such as chemical constitution, density or particle size, are not readily reduced to metal by the furnace gases.)

In this case, some of the reduction is effected under conditions approaching the oxide-slag iron-bath system previously mentioned, in which the carbon required is only 720 lb. per ton of iron produced. The magnitude of the saving in coke resulting from this condition can be estimated by taking a specific example. Assume that 95 per cent of the reduction is carried out by CO at an effective temperature of 1800° F. (980° C.) and 5 per cent is carried out by carbon in the hearth zone. The minimum amount of carbon required per ton of iron is 0.95 × 1636 + 0.05 × 732 = 1580 lb., or nearly 60 lb. less than if the reduction is all by CO. Under certain circumstances, therefore, it is possible, by having a small amount of direct reduction, to operate more efficiently than by following Grüner's ideal procedure. It is clear, however, that this can be done only if the lessened amount of carbon required, together with the available hot-blast temperature, still suffices to supply the heat needed; that is, if the rate of coke consumption is governed by the use of carbon as a reagent rather than as fuel. Otherwise, a reduction in carbon will reduce the heat supply below the level necessary for continued operation. There are thus obvious practical limitations to having a large amount of direct reaction between carbon and iron oxide, mainly because of the substantially greater supply of heat required for this direct method of ore reduction as compared to indirect reduction by CO.

Heat Requirements

It now remains to see whether the amount of carbon required to provide the necessary reducing gas also suffices to supply the necessary heat. In considering this, we shall pass over for the moment the question of where this heat is produced and consider only the net heat generated in the furnace as a whole. According to the heat balance given by Mathesius,[1] which is reproduced in Table 2, a blast furnace producing the common grades of pig iron requires approximately 13,000,000 B.t.u. for each ton of iron produced, of which close to 11,000,000 are commonly supplied by combustion of coke and the remaining 2,000,000 are brought in by the hot blast. If, therefore, the heat liberated by combustion of the coke required to give the necessary reducing gas is of the order of 11,000,000 B.t.u., or greater, when the carbon is burned so as to give the equilibrium mixture of CO and CO_2, it may be concluded that the coke consumption is determined mainly by the use of carbon as a reducing agent. On the other hand, if the heat thus liberated is less than 11,000,-000, and is so much less that it is not practical to supply the difference by increasing the heat brought in by the hot blast, it may be concluded that the coke consumption is fixed by heat requirements.

Although the temperature at which rate of reduction by CO becomes rapid varies considerably with the nature of the ore, it is not unreasonable

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[1] References are at the end of the paper.

to assume that 1500° F. (815° C.) is somewhere near the lowest temperature at which reduction can be carried on at a feasible rate. The data collected by S. P. Kinney[2] show that not more than 20 per cent of reduced ore is present at the level for which the average temperature is 1500° F. (815° C.), and considering the rapid decrease in rate of reduction with decreasing temperature it is not likely that reduction is occurring very rapidly below this temperature. Even granting that 1500° F. (815° C.) is somewhat higher than the minimum temperature for an economical rate of reduction of FeO, no appreciable error is introduced into the calculations as made.

TABLE 2.—*Heat Balance Sheet for One Ton of Product*
TAKEN FROM MATHESIUS[1]

Generated			Consumed			
By	B.t.u.	Per Cent	By	B.t.u.		Per Cent
Combustion C to CO	3,995,000	31.1	Reduction of Fe_2O_3..	6,133,300		
Combustion C to CO_2	6,754,000	52.6	Reduction of Fe_3O_4..	490,000	6,623,300	
Hot blast (heat content)..............	2,057,000	16.0	Reduction of MnO .		48,400	
			Reduction of P_2O_5...		17,000	
Moisture of the air in hot blast (heat content)..............	42,000	0.3	Reduction of SiO_2...		418,500	7,107,200	55.3
			Calcination of carbonates.............		702,000	5.5
			Dissociation of moisture in blast.......		397,000	3.1
			Carried off with the iron..............		1,142,500	8.9
			Carried off with the slag......		909,000	7.1
			Carried off with the dry top gases......		752,400	5.9
			Carried off with moisture in top gas.....		700,100	5.4
			Radiation, cooling water, and unaccounted for.......		1,137,800	8.8
Total............	12,848,000	100.0	Total............		12,848,000	100.00

Now at 1500° F. (815° C.), each ton of iron produced requires, as we have seen, 1343 lb. of carbon, of which 480 lb. appears in the exit gas in the form of CO_2 and 863 lb. as CO. We may therefore consider the carbon as being in effect burned partly to CO_2 and partly to CO, so that the heat to be credited to combustion, using the same heats of combustion as Mathesius, is 480 × 14450 + 863 × 4453 = 10,820,000 B.t.u., which is very close to the credit of 3,995,000 + 6,754,000 = 10,749,000 B.t.u. made in Table 2. At 1800° F. (980° C.) the carbon required is 1656 lb., of which 480 is in effect burned to CO_2 and 1176 lb. goes to CO, consequently the heat liberated is 480 × 14450 + 1176 × 4450 = 12,210,000 B.t.u.,

which is considerably more than the credit for combustion in Table 2.   It appears, therefore, that with reduction by CO the heat generated by combustion of the coke required to produce the reducing gas is very nearly enough to supply the heat needed in the furnace (using the raw materials and producing the grade of iron described) and that the hot blast, under most conditions, can supply enough heat to make up any deficit and maintain a satisfactory operating heat balance.

If there is some reduction by carbon in the hearth, the heat generated per unit of carbon charge and available for reactions above the hearth is somewhat less, but unless there is a very large amount of such reduction the heat evolved is not enough less to require any revision of this conclusion.   Moreover, the calculations of the amount of carbon required as a source of reducing agent are based on the assumption that reduction is carried out with a gas of which the carbon monoxide content is substantially the same as that of the equilibrium mixture, when, consequently, the rate of reaction would be effectively zero.   In order to have the reduction go on at an economically feasible rate it is necessary to have some excess of carbon monoxide over that required for equilibrium, hence the amount of carbon actually required for reduction is somewhat greater than that calculated for equilibrium conditions and there is a corresponding extra heat supply above that already taken into account. This means that the heat that has to be brought in by the hot blast is somewhat less than that calculated, and gives added assurance that the hot blast can supply the difference between the total heat requirement and the heat supplied by the combustion of carbon to form the actual CO-CO_2 mixture.

These conclusions are, of course, valid only for the production of the common grades of pig iron.   If the furnace is making ferrosilicon or ferromanganese, the heat requirement is considerably greater than that given in Table 1, and in such cases the coke consumption may be fixed by the heat requirement rather than by the necessity of maintaining a reducing atmosphere.   On the other hand, the amount required for reduction would likewise be greater, because the final $CO:CO_2$ ratio would have to be higher, possibly considerably higher; but the requisite basis of calculation for ferrosilicon and ferromanganese is still uncertain, and it would lead too far to discuss this here.

It should be noted in this connection that the heat of combustion of carbon to CO_2 (14,450 B.t.u. per lb.) is so much greater than the heat of combustion to CO (4453 B.t.u. per lb.) that a small change in the $CO:CO_2$ ratio of the combustion gases is accompanied by a relatively large change in the heat evolved.   For example, one pound of carbon burned in such a way that the ratio of CO to CO_2 in the combustion gases is 2.0 liberates 7720 B.t.u., whereas only 7550 B.t.u. are liberated if the $CO:CO_2$ ratio is 2.2.

The relatively close agreement between the heat supplied on combustion by the carbon required to give the necessary excess of carbon monoxide and the heat required for the furnace as a whole shows that the final balance is obtained by means of blast-temperature regulation. It also indicates the high degree to which the management and operation of the blast furnace have been developed, for unless there is a proper selection of the charge, particularly of the fuel, a proper furnace design and proper operating practice, a proper rate of driving, for example, the difference between the heat requirements of hearth and stack zones is so great that a complete balance cannot be achieved by blast-temperature regulation alone. The fact that such regulation is possible is a tribute to the skill of the blast-furnace operator.

Thus far, nothing has been said about the effect on the reduction equilibria of the presence of metals other than iron, such as manganese or silicon, or of metalloids such as phosphorus. Precise data bearing on this point are scarce but it seems likely that the effect of phosphorus and sulphur can be neglected because they are present at a relatively small concentration and that no great error is introduced if it is assumed that manganese acts as if it were iron. On the other hand, silica is generally present in appreciable quantities and has a high heat of reduction to silicon, so that it should be considered. Schenck and Laymann[4] measured the equilibrium of CO and CO_2 over mixtures of iron, iron oxides and silica at 900° C. (1650° F.) with the following results. In the reduction of Fe_2O_3 to Fe_3O_4 and Fe_3O_4 to FeO, the equilibrium concentration of CO was slightly lower in the presence of silica than with the iron oxides alone. ·Equilibrium in the reduction of FeO to Fe appeared to be sensitive to the proportion of iron present; with a ratio of SiO_2 to Fe of 5 to 1 by weight, the equilibrium ratio of CO to CO_2 was approximately 5.6, which is considerably higher than that in the absence of SiO_2, whereas if the ratio of SiO_2 to Fe was 1 to 5 the equilibrium ratio of CO to CO_2 was identical with that over FeO and Fe alone. Moreover, no detectable reduction of silica occurred until an appreciable quantity of iron was present. These observations indicate then that if the ratio of Fe to SiO_2 is high, as it must be over a large portion of the lower part of the furnace, SiO_2 has little effect on the equilibrium in the reduction of FeO by CO. Such influence as there is, however, is in the direction of increased carbon consumption, and although we shall neglect it in this preliminary survey, it may well be that when more accurate data on blast-furnace operation are available and a more precise calculation is attempted the effect of silica will have to be taken into account. Schenck[4] gives further data on the reduction of silica itself under blast-furnace conditions, which indicate that this reaction takes place chiefly between silica as a component of molten slag and molten iron saturated with carbon, and that the final silicon content of the iron is determined chiefly

by the temperature of the molten iron in the hearth and the composition of the slag. As a consequence the amount of carbon required to supply both the reagent and the heat necessary to reduce this silica is not a fixed amount but varies widely, and about the best that we can do is to assume that it is greater but of the same order of magnitude as that required to reduce an equivalent amount of iron.

It should be noted that as the hearth temperature is effectively fixed by the composition of iron and the slag being produced, and as the hearth temperature is an important factor in determining the coke rate, there is a direct relation between the composition of the pig iron produced and the coke consumption.

This discussion has also neglected the 3 or 4 per cent of carbon contained in the molten pig iron, but this omission is largely compensated for by the fact that the preceding calculations are based on a ton of pure iron rather than on a ton of pig iron. For example, the carbon consumption for 1600° F. (871° C.) as given by curve 1 in Fig. 2 is approximately 1450 lb. per ton of pure iron. The carbon consumption for a ton of pig iron containing 94 per cent iron and 4 per cent carbon is therefore $1450 \times 0.94 = 1363 + 2240 \times 0.04 = 89$, or a total of 1452 lb. of carbon, which is substantially the same as the requirement given by the curve for pure iron. When allowance is made for carbon required to reduce other oxides, such as SiO_2, MnO and P_2O_5, this consumption is slightly increased, but the values given in Fig. 2 can be taken as a good first approximation when considering either a ton of pure iron or a ton of pig iron. It should be noted that these values are for iron actually reduced, and a furnace charging an appreciable quantity of scrap can obviously show a considerably lower consumption.

In pig-iron production we are thus justified in regarding the carbon consumption as set primarily by the amount required for reduction, and it is of interest to estimate what the efficiency of an actual furnace is on this basis. In making such an estimate the data in Fig. 2 are useful and lead to some fairly definite conclusions. First, it is obvious that the higher the temperature at which the reduction is carried out, the higher is the coke consumption. It is therefore desirable from the standpoint of coke consumption to operate at as low a reduction temperature as other factors permit. Second, many modern blast furnaces are operating at a very high efficiency, as is evident if an approximate calculation of the efficiency is made on the basis of curve 2. Reduction in the blast furnace does not occur at a single temperature, and there is even a difference of opinion as to the temperature range in which most of the reduction does take place, but for the purpose of this calculation no great error is introduced if it is assumed that most of the reduction is carried out at a temperature of 1600° F. (871° C.), which is probably close to the mean temperature of the reduction zone. An appreciable fraction of the total

reduction occurs above this temperature, and thus requires more coke per ton of iron than the part reduced at 1600° F. (871° C.). On the other hand, there can be no doubt that some reduction occurs below 1600° F. (871° C.) and as such low-temperature reduction requires less coke than is necessary at 1600° F. (871° C.) this tends to offset the larger amounts required in high-temperature operation. The temperature 1600° F. (871° C.) is therefore believed to be a fair basis for the estimate. Neglecting the possibility of direct reduction in the hearth, the minimum coke consumption as taken from Fig. 2 is about 1600 lb. per ton of iron produced from ore. Consequently, a furnace using 1700 lb. of coke is operating at close to 95 per cent efficiency, and a furnace using 1800 lb. of coke is about 90 per cent efficient. If the furnace is operated in such a way that the reduction of FeO to Fe is carried out at a lower temperature, the coke consumed is correspondingly less, and the fact that a coke rate of 1460 lb. has been achieved in practice, although under rather special conditions, shows that such low-temperature reduction with a very high efficiency is possible, and that it is economical as far as coke consumption is concerned. It may not be economical, however, if one considers the output of the furnace and the return on the capital invested. These efficiencies, of course, are only estimates based on many assumptions, but as the assumptions are reasonable the conclusions based upon them can be used with some confidence.

It is also evident that the faster a furnace is driven the less chance there is for the attainment of equilibrium, or true countercurrent operation, hence the coke rate should, and in fact does (within reasonable practical limits), increase with the rate of production of iron. In striving to achieve most economical operation with a given furnace, it is therefore necessary to balance the rate of production against the cost of coke, which is an interesting problem but one that is outside the province of this discussion.

Furthermore, since the efficiency of modern furnaces is over 90 per cent, based on the performance of the perfect furnace, it is clear that the more complicated devices now being promoted by inventors have little, if any, chance of producing a spectacular reduction in the coke consumed per ton of iron. This, of course, does not mean that no improvement in blast-furnace practice is possible. On the contrary, it is safe to predict that advances can and will be made, but if the interpretation just given is correct the improvements will be more in the form of closer control to secure a more uniform product than in any marked reduction of coke consumption below that of the best practice at present. Summarizing these conclusions, we find: first that the ultimate lower limit of coke consumption for pig iron is in most cases determined by the chemical equilibrium of the reduction reactions, particularly by the equilibrium over FeO and Fe; second, that the carbon consumption decreases with

the temperature of the reduction; consequently, greatest economy is obtained by carrying on the process at as low a temperature as is connected with a satisfactory over-all rate of production of iron. Finally, if our interpretation is correct, the relative efficiency of a modern blast furnace, defined as the ratio of coke consumed by the perfect furnace to that consumed in the furnace in question, is remarkably high. The exact value is difficult to estimate because in actual operation metal is produced not at a single temperature but over a range of several hundred degrees, but the indications are strong that many modern furnaces are operating at over 90 per cent of their maximum theoretically possible efficiency.

The relatively high efficiency indicated by the coke consumption implies that many furnaces are working rather close to equilibrium. Further evidence to support this deduction is found in the agreement between direct measurements made by Kinney[3] of the gas composition at four different levels in the stock column of a commercial furnace and the $CO:CO_2$ ratio at equilibrium as calculated from Fig. 1 and from the operation of the perfect furnace. This agreement is shown in Table 3, in which the first column gives the position for which the data apply, expressed as distance from the wall at the given level, the second column gives the temperature at that point, as read from Kinney's curves, the third gives the ratio of CO to CO_2 as calculated from his data, and the fourth gives the equilibrium ratio of CO to CO_2 for the temperature given in the second column as calculated from the data of Fig. 1. The gas composition is expressed as the ratio of CO to CO_2 rather than in percentage of CO or CO_2, for two reasons: (1) to emphasize that the important point is the value of this ratio; (2) to avoid any confusion resulting from the fact that the actual furnace gas contains a large percentage of nitrogen, which is without effect on the equilibrium.

At plane 4, the hottest level investigated, there was always an excess of CO above that required for equilibrium over Fe and FeO, as, of course, there must be if rapid reduction to metallic iron is taking place. At plane 3, the observed ratio shows surprisingly good agreement with the equilibrium ratio over the whole distance investigated. It is true that the furnace gas contains slightly less CO than is required at equilibrium but in view of the difficulty in making observations and of the sensitivity of the ratio to small changes in composition in this range, the difference is not great and the data can be taken as indicating that at this level equilibrium had been substantially attained. At plane 2, the CO content is definitely below that required for equilibrium over FeO and Fe, but is appreciably above the CO concentration at equilibrium over Fe_3O_4 and FeO. This means that at this level the gas can reduce Fe_3O_4 but not FeO; indeed, it is oxidizing in relation to iron and will tend to convert any reduced metal back to ferrous oxide. The most interesting point

TABLE 3.—*Comparison of $CO:CO_2$ Ratio in Different Parts of a Blast Furnace*

As Reported by Kinney with Ratio at Equilibrium

Location, Feet from Wall	Observed Temperature, Deg. F.	Observed Ratio of CO to CO_2	Equilibrium Ratio of CO to CO_2 (Fig. 1)	
			Over Fe-FeO	Over FeO-Fe_2O_4
PLANE 1 (6 FEET BELOW STOCK LINE)				
1	450	2.1		1.0
2	575	1.4		1.0
3	740	1.3		1.0
4	880	1.3		1.0
5	1040	1.4		1.0
6	1180	1.4		1.2
7	1300	1.7		1.5
8	1325	4.2		1.6
PLANE 2 (14 FEET BELOW STOCK LINE)				
1	1100	2.1	1.0	0.9
2	1000	1.4	1.0	1.0
3	1200	1.4	1.3	0.7
4	1550	1.4	2.3	0.3
5	1600	1.4	2.3	0.3
6	1625	1.4	2.3	0.2
7	1625	1.4	2.3	0.2
PLANE 3 (24 FEET 7 INCHES BELOW STOCK LINE)				
1	1575	1.9	2.0	
2	1375	1.3	1.7	
3	1625	1.8	2.2	
4	1650	1.8	2.3	
5	1650	1.8	2.3	
6	1650	2.0	2.3	
7	1700	2.2	2.3	
PLANE 4 (47 FEET BELOW STOCK LINE)				
1	1400	99.0	1.7	
2	1650	19.0	2.3	
3	1840	4.9	2.6	
4	1900	3.5	2.7	
5	1875	3.2	2.6	
6	1750	3.5	2.4	
7	1800	3.8	2.4	
8	1850	4.0	2.6	

about the data for this plane, and those for plane 1 as well, is that the ratio is constant at approximately 1.4, which corresponds in a mixture of pure CO and CO_2 to 58 per cent carbon monoxide, because it was shown in an earlier section that in the perfect furnace the CO content was not reduced below 52 per cent (or a ratio of 1.1). The exact concentration of CO remaining in the gas in an actual furnace obviously depends on the speed at which the gas passes over the ore, but the fact that the CO content of the gas in the furnace approaches that of the gas in the perfect furnace so closely indicates that equilibrium and true countercurrent operation in the stock column are likewise approached.

We have thus far considered the operation of the perfect furnace and have rated the performance of an actual furnace in terms of the operation of the perfect furnace. It now becomes of interest to see how the operation of an actual furnace departs from that of the perfect furnace and to determine how departures from equilibrium and the occurrence of side reactions influence the efficiency. It has already been shown that the necessity of operating with an excess of carbon monoxide above the concentration of equilibrium in order to make the reaction proceed at a reasonably rapid rate leads to an increased consumption of carbon with consequently less efficiency. Failure to operate under true countercurrent flow, which is simply another way of saying that equilibrium is not attained, for true countercurrent flow implies equilibrium at every point in the furnace, leads to an increased consumption of carbon. One of the commonest causes of deviation from countercurrent operation is the tendency for the reduced iron shell surrounding each lump of ore to sinter, thereby making it much more difficult, sometimes effectively impossible, for the reducing gas to reach the unreduced oxide core. Another cause for lower efficiency is the occurrence of side reactions, particularly the so-called solution reaction $CO_2 + C = 2CO$. This reaction has definite equilibrium just as do the oxide reductions, so that at each temperature there is a particular ratio of CO to CO_2 that is not altered by long contact with carbon. (The equilibrium ratio in this case is also influenced by the partial pressure of both CO and CO_2 but since this effect is small compared to that of temperature it is neglected here.) If the composition of the gases differs from this ratio, reaction occurs in such a way as to make the composition approach that at equilibrium. Equilibrium compositions as determined by experiment are given by the dashed line in Fig. 1 and show that at temperatures above 1400° F. (760° C.) the percentage of CO that can exist over carbon is greater than that required for equilibrium over FeO and Fe. Consequently, if the composition of the gas lies within the range represented by the field BCD, FeO is reduced and CO_2 reacts with C to give CO. As the temperature increases this field widens so that the chance for loss of carbon by solution increases. Actually, the net result is controlled by

the relative rates of the two reactions, whose magnitude it is not possible to predict. But it can be said that both rates increase with temperature and experience indicates that the rate of reaction of CO_2 and C increases somewhat faster than the rate of reduction, particularly at an iron surface, hence high temperatures lead to increased solution loss for two reasons: (1) because of unfavorable equilibrium conditions and (2) because of increased rate of reaction. On the other hand, as the gases cool, the equilibrium shifts so as to cause a deposition of carbon, but the rate also decreases so that the amount of carbon actually deposited depends on the relative rates of cooling the gases and of reaction.

The conclusions as to the role of equilibrium in blast-furnace operation also have a bearing on the advantages, if any, to be gained by oxygen enrichment of the blast. So far as coke consumption is concerned, these advantages appear to be small if the furnace is working close to equilibrium. As oxygen itself does not enter into the reduction reaction, it can have no effect on the equilibrium, consequently the performance of a furnace working close to equilibrium conditions cannot be improved by having a higher concentration of oxygen in the blast. The only way oxygen can affect the process is by providing a higher combustion temperature and by giving a better control of the hearth heat, but these adjustments can usually be made more simply by changing the blast temperature. If, however, the furnace were making ferromanganese or ferrosilicon, which require a high hearth temperature and a large heat supply, an oxygen-enriched blast would probably be helpful, if economically practicable.

There is also evidence indicating that oxygen is beneficial in a furnace with a high coke consumption; for example, Lennings,[5] in a careful experimental study on a furnace of 50 to 60 tons of iron per day, found that when the coke consumption was 2000 to 2200 lb. per ton of iron it could be lowered 200 to 300 lb. by the use of an enriched blast although extra oxygen was of little value when the coke consumption was normally low. This last observation is just what would be expected, since the closer the approach to the minimum fuel consumption set by equilibrium the less will be the effect of changes in blast composition. It is difficult to avoid the conclusion that in a furnace using 2000 lb. or more of coke per ton of iron an equivalent reduction in coke rate can be made by correcting faulty phases of operation or by increased blast temperature rather than by adding oxygen to the blast.

THERMAL EFFICIENCY OF THE BLAST FURNACE AS A SMELTER

In considering the thermal efficiency of the blast furnace, it is difficult to set up standards as definite as for material efficiency. It is possible, however, to come to a definite conclusion on certain points pertaining to the calculation of thermal efficiency. For example, since the primary

function of the furnace is to produce a highly reducing gas, it is not logical to charge the furnace with the full calorific value of the fuel, that is, with the heat evolved on complete combustion to CO_2—for the perfect furnace, it should be charged with the heat of combustion to CO, and for a real furnace, with the heat actually evolved.   The efficiency based on charging the furnace with heat generated in the furnace plus the heat in the blast and crediting it with useful heat work done in the furnace, including sensible heat in molten iron and slag, is, according to Joseph,[6] usually over 80 per cent; Mathesius' heat balance[1] shows an efficiency of over 80 per cent for his furnace.   This high efficiency is obtained because the blast furnace is a recuperator with relatively high transfer of heat from gas to stock.   The only loss is in sensible heat in top gas and cooling water, and in radiation from the walls, which Marhsall[7] has shown to be small.

It should be noted that the blast furnace utilizing 80 per cent or more of the thermal energy supplied to and generated in it is a much more efficient piece of apparatus than, for instance, the open-hearth furnace, which has a thermal efficiency of the order of 20 per cent.

Material Efficiency of the Blast Furnace as a Gas Producer

The purpose of the gas producer is to make a combustible gas high in carbon monoxide, by the incomplete combustion of carbon, therefore if we consider iron as a by-product we may look upon the blast furnace as essentially a large gas producer.   The top gas leaving the furnace is the gas considered, because this is the gas that is used as fuel.   The hearth of the blast furnace is a very efficient gas producer because the gas leaving it has substantially no CO_2, but this gas is not available for use outside the furnace.   At first glance the fundamental chemical reaction of the producer appears to be

$$C + \tfrac{1}{2}O_2 = CO$$
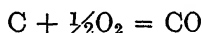
but the composition of the gas—that is, the relative amount of CO and CO_2 produced—is actually determined by equilibrium in the reaction:

$$C + CO_2 = 2CO$$
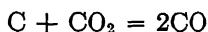
This reaction is identical with the solution reaction of the blast furnace, so that the amount of CO obtained varies with temperature in the manner shown by the dashed curve in Fig. 1.   (As before, we shall neglect the effect of changes in partial pressure and shall assume that the process is carried out substantially at a partial pressure of one atmosphere.)   This curve shows that the proportion of CO in gas from an ideal producer increases with the effective temperature of operation and approaches 100 per cent only at temperatures above 1800° F. (or 1000° C.).   There-fore, in considering the efficiency of a blast furnace as a gas producer,

we should base the calculation not upon complete conversion of carbon to CO but upon the maximum amount of CO yielded by the ideal gas producer at the temperature considered. The efficiency so obtained we shall call the relative efficiency. Now Fig. 1 shows that at temperatures above 1450° F. (790° C.) the equilibrium concentration of CO for the producer reaction is greater than that for the reduction of FeO to Fe, which, as already said, is the controlling reaction in the blast furnace. This means that in this temperature range the blast furnace must in principle be less efficient in converting carbon to CO than the gas producer. The maximum efficiency of the ideal producer is entirely analogous to that of the Carnot cycle efficiency of a steam engine in that it tells us what the maximum yield will be for a given temperature of operation, and the relative efficiency of the blast furnace is then comparable with the efficiency of an engine operating on some cycle that is less efficient than that of the Carnot engine.

In order to obtain an idea of the magnitude of this relative efficiency, the yield of carbon monoxide per ton of carbon consumed has been calculated for the gas producer and for the blast furnace, making the reasonable assumptions that the controlling equilibrium in the blast furnace is that for the reaction $FeO + CO = Fe + CO_2$ and that both gas producer and blast furnace operate substantially at equilibrium. The results (Table 4) indicate that the blast furnace is in principle only about 70 per cent as efficient as the gas producer. It should be noted that as the

TABLE 4.—*Relative Efficiency of Blast Furnace as Gas Producer Based on Pounds of CO Produced per Ton of Carbon*

Temperature	CO per Ton, Lb.		Relative Efficiency, Per Cent
	Ideal Gas Producer	Ideal Blast Furnace	
1500° F. (810° C.)...............	3735	3000	80
1650° F. (900° C.)...............	4480	3170	71
1800° F. (980° C.)...............	4600	3300	71

temperature is lowered the relative efficiency of the blast furnace as a gas producer increases, and according to Fig. 1 may exceed 100 per cent at temperatures below 1450° F. (790° C.). This means that if the process could be carried out at such a low temperature, which is, of course, neither desirable on other grounds nor economically feasible, the blast furnace would yield a better gas than the producer.

It should be noted that if equilibrium in the reduction reaction is not attained—that is if the gases contain more CO than the equilibrium requirement—the assumptions inherent in the calculation of the relative efficiency are not met and the apparent relative efficiency of the blast

furnace as a gas producer may exceed 100 per cent. Moreover in any actual case it is possible though not likely that failure to attain equilibrium may give the blast furnace a higher efficiency than the gas producer operating at the same temperature.

The usefulness of the gas produced has a great deal to do with the economical operation of the furnace because the credit for gas burned in the stoves, soaking pits and elsewhere is considerable; furthermore, it is evident that any new process designed to compete with the present blast furnace must also have a high efficiency as a gas producer, a fact that frequently is overlooked by promoters of such schemes.

THERMAL EFFICIENCY OF BLAST FURNACE AS A GAS PRODUCER

The thermal economy of a gas producer in the sense of heat generated that is not lost by radiation in cooling water, etc., clearly depends entirely on the design and cannot be idealized as can the material efficiency. It is, however, customary[8] to consider the thermal efficiency in terms of the calorific value of the gas produced, and on this view a comparison of gas producer and blast furnace can readily be made. The so-called cold-gas efficiency of the producer as ordinarily used is defined as the ratio of the calorific value of the gas produced per ton of carbon to the calorific value of the carbon itself. Since the calorific value of the gas depends on the proportion of CO present, which varies with temperature, the efficiency will vary with temperature. The calorific value of one ton of carbon is approximately 28,000,000 B.t.u., while the calorific value of CO is about 4500 B.t.u. per pound of CO. Taking the data of Table 1 for the CO produced per ton of carbon, the cold-gas efficiency of the ideal producer varies from about 60 per cent at 1470° F. (800° C.) to nearly 75 per cent at 1800° F. (1000° C.). The cold-gas efficiency of the ideal blast furnace based on the data in Table 1 is approximately 70 per cent of that of the ideal gas producer and ranges from 42 per cent at 1470° F. to 52 per cent at 1800° F. (1000° C.). The actual cold-gas efficiency of a blast furnace based on flue-gas analyses is usually within the range given and indicates, as did the material efficiency, that the blast furnace is working close to maximum possible efficiency.

It is also of interest to consider the hot-gas efficiency of the gas producer, which Hirshfeld and Barnard[8] define as the sum of the calorific value of the gas and the sensible heat of the exit gases divided by the calorific value of the fuel used, or:

$$\text{Hot gas efficiency} = \frac{\text{calorific value of gas} + (\text{heat generated} - \text{losses})}{\text{calorific value of fuel}}$$

Obviously, the only inefficiency here is the heat lost by radiation, in cooling water, etc., and since this is only a fraction of the heat generated

in the producer its value will not be large. Furthermore, equilibrium does not enter into this calculation because the loss in calorific value of the gas through presence of CO_2 is exactly balanced by heat liberated in the furnace through reaction combustion to CO_2. Hirshfeld and Barnard,[8] assuming that 20 per cent of the heat generated on the process is lost by radiation, etc., found the hot-gas efficiency of a gas producer to be about 94 per cent. The blast furnace will not quite achieve so high a figure because of loss of heat in the molten iron but its efficiency should be very close to 90 per cent. It should be noted, however, that this efficiency implies recovery of the sensible heat in the waste gases—a process that is done by the blast furnace chiefly in the furnace itself, whereas the gas producer frequently requires some other equipment to utilize this energy.

Summary

A consideration of the material and thermal efficiencies of the blast furnace considered both as a smelter and as a gas producer leads to the following conclusions:

1. In a blast furnace producing the usual grades of low-silicon pig iron, the coke consumption is determined by the demand for carbon as a reducing agent rather than the demand for fuel, for the heat liberated on combustion by the carbon necessary to give the proper quantity of reducing gas, is, together with the heat brought in by the hot blast, sufficient to meet the heat requirements of the furnace. The general heat balance as well as the distribution of the heat generated between hearth (melting) and shaft (reducing) zones is controlled within limits by adjusting the temperature and volume of the hot blast. If the furnace is producing high-silicon foundry iron, ferromanganese or ferrosilicon, the heat requirement per ton of product is considerably greater than for the ordinary pig-iron grades and the coke consumption may be fixed primarily by the demand for carbon as fuel, although this may not always be true since the $CO:CO_2$ ratio at equilibrium is also raised in such cases.

2. The amount of coke required for giving a proper reducing gas is fixed chiefly by the equilibrium conditions in the reduction of FeO to Fe, and, since the equilibrium changes with temperature, the coke consumption is likewise influenced. The higher the temperature at which this stage in the reduction is carried out, the higher the coke consumption.

3. Preliminary calculations taking account of the chemical equilibrium indicate that a blast furnace using 1800 lb. of coke per ton of pig is over 90 per cent efficient in the utilization of coke.

4. The thermal efficiency of the blast furnace taken as a smelter is high, being usually better than 80 per cent.

5. Taking the blast furnace as a gas producer, the maximum conversion of coke to carbon monoxide must be less than that of a gas producer, the relative efficiency being in the ideal case about 70 per cent. An actual

blast furnace usually operates close to its own ideal efficiency as a producer, however.

6. The hot-gas efficiency of the blast furnace regarded as a gas producer is high, being of the order of magnitude of 90 per cent.

7. These conclusions all indicate that the blast furnace as now operated is a relatively efficient apparatus compared to other chemical or metallurgical equipment. While improvements in design, in control of operation to give a uniform product, and in reducing heat loss by radiation and conduction are to be expected, there is little hope of making a substantial reduction in coke consumption under that achieved by the best modern practice. It is also clear that any process designed to compete with the blast furnace must, like the blast furnace, show a high efficiency both as a smelter and as a gas producer if it is to have any chance of success in competition with the blast furnace in the steel-producing districts, where metallurgical fuel, suitable for blast-furnace use, is commercially available.

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DISCUSSION

(George B. Waterhouse presiding)

T. L. JOSEPH* Minneapolis, Minn.—Mr. Austin, do you really think 13,000,000 B.t.u. of heat are liberated in the furnace for making a ton of pig iron?

J. B. AUSTIN.—No, not necessarily. That is only a heat balance on the basis of what goes in and what comes out. It is a matter of bookkeeping. I am not saying anything about how much heat appears at any given point in the furnace. So much coke comes in and so much carbon monoxide and dioxide come out, and it is assumed that a corresponding amount of heat was liberated by this formation of CO and CO_2.

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* Professor of Metallurgy, Minnesota School of Mines and Metallurgy.

I could actually go through the calculations of the heat requirements for each of these reactions, but it is complicated and it is much simpler for this purpose to take just what comes in and goes out.

T. L. JOSEPH.—I think Mr. Austin's is a very good paper, because it attacks blast-furnace operation from a fundamental point of view. My only point was that in figuring heat balances ordinarily we consider the top gas to contain so many pounds of CO_2 and so much CO; we say that the CO_2 is formed by burning so many pounds of carbon and that heat is liberated accordingly. Actually, the CO_2 is largely formed by the reduction of iron oxides and calcination of limestone. A small amount of heat is liberated when CO_2 is formed by indirect reduction. The usual heat balance gives an erroneous conception as to the amount of heat that is actually liberated in the blast furnace per ton of pig iron. Practically all the heat is generated at the tuyeres. If we get a proper conception as to the amount of heat actually liberated in the furnace, we begin to appreciate more fully the effect of blast temperature on the control of the operation.

The primary concern of blast-furnace operators, day in and day out, is to control the silicon and the sulphur in the iron. The operator adjusts the amount of coke and blast temperature to control the amounts of these elements in the iron.

The carbon required in Lake ore practice is fixed pretty definitely by the temperature required in the hearth to control silicon and sulphur. When the temperature requirements are satisfied, the gas in the lower part of the furnace will have ample reducing power. That is, the gas will contain CO in excess of the equilibrium concentrations at the temperatures prevailing in the lower part of the furnace.

In the last analysis, the coke requirements for a given set of raw materials depend upon the control of temperature in the hearth to control the silicon and sulphur in the iron.

This work shows that the gas in plane four and below contained more than twice as much CO as CO_2. As I recall, there was about three or four times as much CO.

J. B. AUSTIN.—I am perfectly willing to admit that to control the furnace it is necessary to control the place where the heat is liberated. That is not what I am striving to find out. I am striving to find out the smallest amount of coke required for reduction.

As to the question about the composition of the gas coming out of the bosh, I believe that the gas leaving the hearth is practically all CO.

R. A. LINDGREN,* South Chicago, Ill.—Mention was made of high blast temperature and its apparent effect of lowering the coke consumption. Has Mr. Austin reconciled the fact that the Gary Works of the Carnegie-Illinois Steel Corporation have run consistently the lowest coke per ton of iron of all the Corporation's plants, but have nevertheless carried the lowest blast temperature?

J. B. AUSTIN.—As a matter of fact, I did not say anything about blast temperature, but I fail to see that the temperature of the incoming blast controls the temperature at which the reduction takes place, the effective temperature of reduction. I am not a blast-furnace operator, but I am not completely convinced that blast temperature is the thing that controls the temperature in the stack where the reduction actually takes place.

G. B. WATERHOUSE,† Cambridge, Mass.—This is based on Fe_2O_3 ore and many of us are using that. How is that going to affect this?

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* Superintendent, Blast-furnace Dept., Wisconsin Steel Works, International Harvester Co.

† Professor of Metallurgy, Massachusetts Institute of Technology

J. B. AUSTIN.—That raises the amount of carbon required. All these things that you mention increase the consumption of coke because nobody under ordinary operation gets any such coke rates as these.

T. L. JOSEPH.—The Wisconsin Steel Co., I think, has operated furnaces that made pig iron on 1580 lb. of coke per ton. I believe pig iron has been made on coke rates lower than the theoretical minimum indicated by this paper.[9]

J. B. AUSTIN.—The U.S. Steel Corporation has made iron using only 1460 lb. of coke per ton, but that is slack operation, and it was in effect operating a gas producer.

R. A. LINDGREN.—How much sinter and how much scrap?

J. B. AUSTIN.—I do not know.

C. P. LINVILLE,[*] Bound Brook, N. J.—Was there not a furnace test on the operation in which for a month the average was something like 1370?

R. A. LINDGREN.—That was with a 60 per cent sinter charge.

C. P. LINVILLE.—Of course, if you lower the temperature, you can better this figure.

J. B. AUSTIN.—Yes, that is true, but you might not be able to do it profitably. Mr. Avery has a way, he thinks, of getting faster reduction at lower temperature,[†] so if he can reduce the effective temperature at which reduction is carried out, he can lower the coke consumption appreciably. It is also true that if you have a small amount of direct reduction taking place in the hearth, say, 5 per cent, you can reduce the values I gave a little more. I did not bring that up in the presentation of the paper because of the lack of time.

R. A. LINDGREN.—Howland could not balance the carbon available in the furnace without going to some direct reduction—in other words, disrupting the ideal working conditions. Have you calculated a balance on that ideal furnace of yours?

J. B. AUSTIN.—Yes.

R. A. LINDGREN.—Assuming a small amount of direct reduction?

J. B. AUSTIN.—I think it was 5 per cent direct reduction. That may be low. I did not calculate the carbon balance, but the heat that would be obtained with some direct reduction.

R. A. LINDGREN.—Getting back to the high temperature, do you suppose the higher blast temperature would affect somewhat the percentage of direct reduction, thereby affecting the lower coke rate?

J. B. AUSTIN.—It might. I must confess that the question of direct and indirect reduction is somewhat of a mystery to me. I do not understand what different people mean by direct and indirect reduction. Some people talk about direct reduction occurring in the stack; others, talk about direct reduction occurring only in the hearth.

If one could operate a furnace with a bath of molten iron saturated with carbon and an iron oxide slag on top he could cut this figure in half. But such operation requires an external source of heat.

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[9] Howland: *Trans.* A.I.M.E. (1916) **56**, 342.

[*] Metallurgist, The Calco Chemical Co.

[†] See page 102, this volume.

T. L. JOSEPH.—It seems to me that a significant fact, brought out most distinctly by Mr. Austin, is that if reduction is completed at low temperatures there is a distinct advantage. The gas contains less CO and still is reducing. Solution loss and direct reduction will be minimized. This is the ideal toward which we are all working; i.e., to reduce the iron ore completely in the top of the furnace at lower temperatures.

If the ore is reduced in the lower part of the furnace, either with carbon direct or with CO forming CO_2, which in turn reacts with the coke forming CO, that means a loss of thermal efficiency. To reduce the ore in the upper part of the furnace requires a uniform gas distribution to get the ore and gas in contact for preheating as well as for reduction.

J. B. AUSTIN.—I am in entire agreement with Mr. Joseph on this point.

Pressure Operation of the Pig-iron Blast Furnace and the Problem of Solution Loss

By Julian M. Avery,* Member A.I.M.E.

In its dual role of pig-iron smelter and gas producer, the blast furnace is a remarkably satisfactory and efficient apparatus. Many metallurgists and engineers have pointed out, however, that since the primary function of the blast furnace is to produce pig iron at the lowest possible cost, its function as a gas producer should be subordinated to this primary purpose. During the past 10 years or more, improvements in blast-furnace technique and economy have, in fact, been directed primarily to increasing efficiency in the use of the reducing power of the gases produced by combustion of coke at the tuyeres, to reduce iron ore within the furnace. The net over-all result is a decrease in the fuel value of the top gas per unit of volume, and per ton of pig iron, which is evidently more than offset in value by the corollary saving in coke and the possibility of increased furnace capacity, for otherwise there would be no point in making such improvements.

The purpose of the present paper is to suggest that, while progress has been made in this direction, there is another approach to the problem of increasing the chemical and thermal efficiency of the blast furnace in its primary role as a pig-iron smelter, which appears to offer possibilities of improvement in over-all economy of a different order of magnitude than results thus far obtained by the use of other expedients. The present argument is based in large part upon the hypothesis that the efficiency and economics of pig-iron smelting are seriously and adversely affected by the phenomenon known as "solution loss," and that the problem of solution loss can be successfully attacked by increasing the over-all pressure; i.e., the "top pressure" under which the furnace is operated. It is indicated that pressure operation may also be expected to result in concomitant benefits, which may be summed up as generally improved operating conditions, together with a substantial saving in fuel and/or a substantial increase in furnace capacity.

In a broad sense, the suggestion of pressure operation of the pig-iron blast furnace is not new, for operation under moderately increased over-all pressure was suggested as early as 1871, by no less an authority than

Henry Bessemer.[1] But the reasons set forth at that time for the use of higher over-all pressure were evidently inadequate, because there appears to be no record that Bessemer's suggestion was ever put to trial. In any event, since blast-furnace literature of at least the past 20 years is singularly lacking in mention of pressure operation, the subject may now be revived from a fresh point of view, as a matter of real and timely significance.

PROBLEM OF SOLUTION LOSS

At about the same time that Bessemer proposed pressure operation, Gruner[2] propounded his theorem of the "ideal" blast furnace, which states with admirable simplicity that a blast furnace operates most efficiently when a maximum proportion of the fuel fed is burned at the tuyeres; i.e., in present-day parlance, when there is no "solution loss." This theorem was apparently viewed with scepticism for many years, but it was revived by Johnson[3] in 1918, and may be said to have been the inspiration for most of the recent progress in blast-furnace technique as exemplified by the splendid work of the U. S. Bureau of Mines.

Theoretical realization of Gruner's "ideal" blast furnace requires that all reduction of iron oxide be accomplished by reaction with CO (or H_2) to form CO_2 or (H_2O):

$$Fe_2O_3 + CO = 2FeO + CO_2 + 7200 \text{ cal.} \qquad [1]$$

$$2FeO + 2CO = 2Fe + 2CO_2 + 4600 \text{ cal.} \qquad [2]$$

$$\overline{Fe_2O_3 + 3CO = 2Fe + 3CO_2 + 11,800 \text{ cal.}}$$
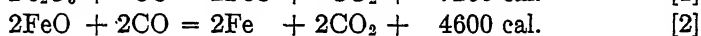
(For the sake of simplicity, Fe_3O_4 may be treated as the intermediate compound $FeO.Fe_2O_3$.)

It has long been known that in actual furnace operation a considerable proportion of the CO_2 thus formed reacts with carbon to form CO:

$$CO_2 + C = 2CO - 41,600 \text{ cal.} \qquad [3]$$

which reaction not only "dissolves" carbon into the furnace gases, but also absorbs a very large quantity of heat.

It is further probable that in many furnaces considerable iron oxide is reduced directly by reaction with carbon to form CO:

$$FeO + C = Fe + CO - 39,300 \text{ cal.} \qquad [4]$$
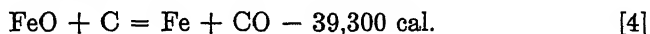
which likewise has the effect of "dissolving" carbon and absorbing a large quantity of heat.

Reactions 3 and 4 are, then, the "solution-loss reactions," and the degree to which they are avoided determines the closeness of approach to

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[1] References are at the end of the paper.

Gruner's theoretical ideal of maximum chemical and thermal efficiency in blast-furnace operation.

From a consideration of these reactions, Johnson[3] pointed out, in 1918, that avoidance of solution loss requires that the ore be reduced to metal as high in the furnace shaft as possible, and that the hearth (bosh) of the furnace should not be called upon to do any chemical work and preheating that can be accomplished in the shaft.

Joseph[4,5] carried the idea further, in 1927, by showing that if the ore is reduced by CO with formation of CO_2 at temperatures below about 1000°C., the reaction of the resultant CO_2 with carbon is so slow, and the linear velocity of the gases so great, that most of the CO_2 formed reaches the top of the furnace without being reduced to CO; which is merely another way of saying that if the ore can be completely reduced before it reaches a zone of temperature as high as 1000°C., solution loss will be nearly, if not quite, eliminated. The same consideration, of course, applies to calcination of limestone with formation of CO_2.

Since the oxides of manganese and silicon are known to be reduced to metal by carbon or carbon monoxide only at temperatures considerably above 1000° C., there is no obvious means of eliminating or even substantially decreasing solution loss in the production of low-iron content ferroalloys such as ferromanganese, though in such cases other advantages from pressure operation are indicated.

That solution loss is a very real problem in the production of pig iron, and not merely a subject for academic discussion, has been proved by the researches of the U. S. Bureau of Mines and others. It has been established[4–8] that in normal American blast-furnace practice solution loss averages on the order of 300 to 400 lb. of coke per ton of pig iron, or from 15 to 25 per cent of the carbon fed. Moreover, since the solution-loss reactions are strongly endothermic, it is clear that additional coke is required to be burned at the tuyeres to supply the heat thus absorbed. It follows that solution loss very seriously affects blast-furnace operation and economy, and that it has the effect of forcing the blast furnace to operate as a gas producer to an extent far beyond the immediate requirements for pig-iron smelting.

It is, of course, true that the increased consumption of coke, because of the indirect as well as the direct effects of solution loss, is reflected in larger volume and increased heat value of top gases per ton of pig iron. For this reason, solution loss is not as serious a matter as coke-consumption figures alone would indicate, and it is even argued by some that large solution loss is actually desirable. Superficially, this point of view may seem reasonable, for, as Rich has pointed out,[9] blast furnaces are normally overblown, thereby increasing solution loss, for the very good reason that within limits the saving in fixed charges due to increased production, plus the value of top gas, more than offsets the increased cost of coke per ton

of product. But the blast furnace with its appurtenances is a very expensive apparatus, and there are cheaper sources of heat than low-grade fuel gas produced by burning coke in a blast furnace with compressed air. It follows that a blast furnace should be operated not with a view to producing large quantities of fuel gas, but to smelting good quality pig iron with maximum over-all economy, making up any resultant deficiency in by-product fuel gas by means of cheap solid or gaseous fuel.

Recent advances in blast-furnace technique are, in fact, directed to this end, for improved distribution of stock, better sizing of raw materials, increased porosity of ore and the like, all lead to improved gas-solid contact, which hastens reduction of ore in the shaft and thus decreases solution loss,[4-8] and decreases the fuel value of the top gases. It has become evident, however, that while the improvements that can be achieved by such methods are important, they are not sufficiently far-reaching in character to provide a fundamental answer to the problem of solution loss. For if furnace operation is improved and solution loss is decreased to a small extent by such methods, it is then usually economical to increase the blast rate and solution loss, striking a new balance of over-all economy between fixed charges, coke consumption, and value of top gases, at a somewhat higher production level.[9-12]

Alternatively, as Rich has shown,[9] solution loss can be decreased to some extent by slow blowing, but this expedient would appear to be economical only in times of relatively small demand for pig iron.

It seems clear that fundamental research directed toward a change in blast-furnace technique so drastic in character that the harmful effects of solution loss may be overcome to a substantial degree with little or no sacrifice in furnace production, and preferably coincident with an increase in production, might be productive of important results. For reasons that will now be discussed, it appears that pressure operation will provide a fertile field for such research, and for obtaining other important advantages in pig-iron smelting.

CHEMICAL EFFECTS OF PRESSURE

Fundamentally, the present suggestion of pressure operation is based upon the theory that if under a given set of conditions the over-all pressure of the gases within a blast furnace is substantially increased by artificially increasing the top pressure, iron ore should be reduced more rapidly in the furnace stack, and a given degree of reduction should, therefore, be reached at a higher level of the furnace than in normal operation. On the basis of this theory, then, in accordance with conclusions reached by Johnson and by Joseph, as previously set forth, such a change in furnace operation should result in decreased solution loss.

That pressure does increase the rate of reduction of iron ore by carbon monoxide (and hydrogen) is confirmed by the recently published results

of Diepschlag.[13] In connection with studies relating to the production of sponge iron, this investigator exposed small samples of finely ground hard hematite to a stream of carbon monoxide at test temperatures of 400°, 600° and 800° C., and at test pressures of 1, 3, 5, 7 atmospheres absolute for each temperature. While Diepschlag's data, as he himself pointed out, cannot be translated directly from laboratory results into terms of commercial operation, it is reasonable to conclude from the data obtained that, other things being equal, the rate of reduction of iron ore by carbon monoxide is increased at least in proportion to the absolute partial pressure of carbon monoxide (or hydrogen) with which the ore is in contact.

In the blast furnace, however, there are other vital factors to be considered. If pressure increases the rate of reduction of iron ore by reason of increased molecular concentration of carbon monoxide, it is to be expected that pressure will likewise increase the rate of reaction between carbon dioxide and carbon; i.e., that the solution-loss reaction rate will also be increased. It has even been suggested that because of this effect increased over-all pressure on the blast furnace might conceivably increase. the solution loss instead of decreasing it.

Possibly the best way to reach an intelligent conclusion as to what may be expected is to take a specific example of normal furnace operation and examine the immediate result of increasing the top pressure on the furnace, thus increasing the over-all gas pressure, without any change in other conditions. Obviously, one such immediate effect is an increase in the rate of reduction of iron ore in the upper portion of the shaft. The inevitable result is that less oxygen will reach lower zones of the furnace in the form of iron oxide and less CO_2 will be formed deep in the furnace. On the other hand, in the lower levels of the furnace—in the bosh and lower portion of the stack—where the ratio $CO:CO_2$ is normally lower than the equilibrium ratio in contact with carbon, a larger proportion of the CO_2 formed.will react with carbon to form CO. Considered as an isolated reaction, this indicates increased solution loss, but it must be remembered that, to the extent that this reaction is increased, the reducing power of the gases in the upper portion of the stack is likewise increased, which in turn increases the rate of reduction of the ore, and thereby further decreases the amount of CO_2 in the lower portion of the stack. It seems clear, then, that, regardless of the relative importance of the changes in various reaction rates, the net effect of increased pressure must be to reduce iron ore higher in the stack and to decrease solution loss by decreasing the quantity of CO_2 formed in high-temperature zones of the furnace. Obviously, then, for a given increase in pressure, a new chemical balance will be reached within the furnace, leading to decreased solution loss, smaller volume and leaner quality of top gas, and less coke required per ton of pig iron.

The discussion thus far has been limited to the effect of pressure upon reaction rates, but it is important to note that pressure also strongly affects the equilibrium of the solution-loss reaction

$$CO_2 + C = 2CO.$$

Increased pressure, other conditions being equal, obviously shifts equilibrium of this reaction toward the left, and as it is a fundamental principle of chemistry that the rate of a chemical reaction decreases as equilibrium is approached, it follows that pressure has the effect of inhibiting the solution-loss reaction. For this reason, and having in mind Diepschlag's results, it is a fair conclusion that increased pressure will increase the average rate of reduction of iron ore in greater proportion than it will increase the average rate of the solution-loss reaction.

Furthermore, there are other theoretical factors pointing in the same direction. If iron ore is reduced at higher furnace levels, it follows that, on average, because of its shorter path to the top of the furnace, the effective exposure of CO_2 in contact with coke is not increased in direct proportion to the increase in pressure. Moreover, if temperatures at various levels of the furnace are assumed to be substantially the same as in normal operation, CO_2 on average will be produced in lower temperature zones, and the average rate of the solution-loss reaction will be less, not only because of the direct effect of temperature upon the rate of reaction but because lower temperature shifts the equilibrium of the solution-loss reaction very strongly in the direction of increased stability of CO_2.

The weight of argument thus appears to be conclusive, that increased over-all gas pressure will exert a strong effect in the direction of lower solution loss. The precise magnitude of this effect cannot be predicted because of many indeterminate factors, and will certainly vary with operating conditions; it is, therefore, quantitatively determinable only by actual trial under operating conditions. Theoretically, it is possible, by using sufficiently high pressure, to eliminate solution loss entirely; but because of the resultant decreased ratio of $CO:CO_2$ in the top gases, and consequent loss in reducing power and fuel value of the gas, it appears that unless some method of gas enrichment is used a compromise is desirable between operating pressure, over-all fuel economy, and other factors to be considered later, which will show maximum over-all economy with some solution loss.

PHYSICAL EFFECTS OF PRESSURE

Since the physical effects of pressure are readily understood, for the sake of brevity they will be dismissed with scant discussion.

Assuming that solution loss is decreased by pressure operation, it is obvious that, for a given rate of production, the blast rate will be less.

As experience with slow blowing has proved,[9] this means less channeling, less dusting, less pressure drop, and better gas-solid contact.

But pressure also produces favorable effects in its own right. Furnas has shown[14] that the pressure drop of gases flowing through a bed of broken solids varies, for a given mass velocity, inversely as the over-all pressure. From Furnas' formula for the floating of solid particles in a stream of gas, it can be shown that the tendency to dusting, other things being equal, appears to vary roughly inversely as the over-all pressure. Since channeling and dusting are closely interrelated, and the tendency to each is decreased by decreasing the pressure drop, it is evident that increased over-all pressure must have a strong favorable effect upon both of these important factors of blast-furnace operation. The decrease in channeling is also bound to improve the gas-solid contact, and thus, on the average, ensure better heat transfer from gas to solid[15] and increase the probability of proper reduction of the ore high in the stack.

Thus, the physical effects of pressure operation are precisely those advantages toward which recent improvements in raw-materials sizing, distribution of stock, and the like, are directed. In short, pressure operation supplements perfectly other means for improving blast-furnace operation, and is not at all antagonistic to them, but it permits going much farther in this direction than expedients thus far proposed or used.

THERMAL EFFECTS OF PRESSURE

Because of the large thermal effect of the solution-loss reaction, it is evident that any considerable decrease in solution loss must result in an important change in the internal thermal balance of the blast furnace. It is well known that in normal operation solution loss occurs principally in the bosh of the furnace, a zone of which the primary function is to complete the heating of the charge and to melt metallic and nonmetallic materials to form pig iron and slag. Clearly, the absorption of large quantities of heat in the bosh by the solution-loss reaction operates to hold down the temperature of the gases, and thus to prevent the bosh zone from properly carrying out its primary function.

Detailed study of the chemical and thermal balance of a typical blast furnace—e.g., the 700-ton furnace studied by the U. S. Bureau of Mines[16]—indicates that solution loss is in fact probably the root cause of the "shortage of high-temperature hearth heat" discussed by Johnston and others as a serious limitation on blast-furnace capacity and efficiency. In the particular case alluded to, solution loss apparently accounted for about 326 lb. of coke, or 17.3 per cent of the total carbon fed in the charge. It has been calculated that if in this instance iron ore had been completely reduced before it reached the bosh, and 1050 lb. of carbon had

been burned at the tuyeres, instead of 1250 lb., other conditions being substantially the same, a very large surplus of heat would have been available in the hearth and bosh, with the result that the temperature of the gases at the top of the bosh would have been on the order of 1250° C., instead of 940° C. as reported. This increase in effective temperature in the bosh may be taken advantage of to melt the charge to metal and slag on the average much higher in the bosh than in normal operation, which offers obvious possibilities in improved control of desulphurization and quality of pig iron. It also permits increased furnace capacity without encountering the condition known as the shortage of high-temperature hearth heat.

Finally, since it will not usually be desirable to have such a high gas temperature at the top of the bosh, decreased solution loss should permit the use of lower blast temperature, which has the twofold effect of conserving fuel gas for other purposes, and increasing the reducing power of the furnace gases by burning more coke at the tuyeres, though other methods of gas enrichment might be used. In a sense, lowering the blast temperature is equivalent to operating the blast furnace as a gas producer, but only to the extent that such practice is justified by conditions within the furnace, and as has been said, only actual trial in a commercial furnace can determine the optimum balance among economic factors and operating conditions involved.

It seems clear that pressure operation, through its effect upon solution loss, may be expected to cause a drastic change in the thermal balance of the blast furnace, which should permit wider control of pig-iron quality, decreased blast temperature, and increased production from a furnace of given size without encountering a shortage of high-temperature hearth heat.

EFFECT OF PRESSURE OPERATION UPON CAPACITY AND FIXED CHARGES

It must be evident that if solution loss can be substantially decreased by pressure operation, the ratio of ore to coke in the charge—the "burden" —will be correspondingly increased; and if the rate of combustion of coke at the tuyeres is maintained constant, i.e., constant blast rate, it is clear that furnace capacity will be increased. Furthermore, increased burden also increases the effective exposure of ore, on the average, to the action of reducing gases, for at a given instant there is more ore in the furnace. This is another factor that acts in favor of pressure operation as a means of reducing solution loss, for it increases the spread between the direct effect of pressure upon the rate of the solution-loss reaction, and its effect upon the rate of reduction of ore. For these and other reasons, the effect of pressure upon furnace capacity may be expected to be greater than the ratio of increase in pressure used.

As has already been pointed out, the saving in coke due to decreased solution loss may be converted in whole or in part into increased furnace capacity, but because of the favorable physical effects of pressure, such as decreased channeling, dusting, and pressure drop, and improved gas-solid contact, it would seem logical to increase the pressure to such a point that production may be increased to a desired extent, without sacrificing much if any of the possible decrease in coke consumption. From theoretical considerations, it would appear to be possible concurrently to practically eliminate solution loss and double the capacity of a furnace of given size, without requiring prohibitively high pressure. This point is stressed because increased furnace capacity is frequently of greater economic importance than savings in coke, after crediting the value of the top gases, and unless some such point of view is adopted, there will probably be a tendency to use pressure operation merely for the purpose of increasing furnace capacity, thus failing to make full use of the possible advantages of this method of operation.

General Considerations

Within the limits of the present paper it is not feasible to discuss in adequate detail, or even to mention, all of the factors involved in the comparative merits of pressure operation. All that can be hoped for is to stimulate discussion of the subject, leaving for later consideration and research problems that arise. For example, the exact amount of pressure required to bring about a given result under given conditions, the effect of pressure upon decomposition of CO in the upper part of the stack, the amount of blast power required, the amount of power that can be economically recovered by expanding the top gases, and the over-all economics of pressure operation, must be left largely for future investigation. Perhaps it suffices to say here that such factors have been studied so far as is possible without adequate data. It appears that very substantial benefits may be obtained by using top pressure on the order of from 10 to 30 lb. gauge, and that considerably higher top pressures may ultimately be found to be desirable; that pressures required need not seriously affect decomposition of CO; that additional blast power required may in most cases be recovered by expanding the top gases; that furnace production may be very substantially increased and probably eventually doubled by pressure operation; and that combined over-all fuel economy and savings in fixed charges due to increased capacity may ultimately be expected to substantially exceed one dollar per ton of pig iron produced.

In conclusion, it is suggested that pressure operation offers a virgin field for development of blast-furnace design and operating technique, which shows promise of a handsome reward for the expense and effort that must be expended if substantial results are to be achieved.

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DISCUSSION

(George B. Waterhouse presiding.)

J. JOHNSTON,[*] Kearny, N. J.—I had the advantage of discussing Mr. Avery's ideas with him recently, and agree that an increase of pressure will *tend* to increase the rate of reduction. But I find difficulty in believing that the net effect would be as large as Mr. Avery expects it would be, in a furnace with a low coke rate, which there-

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[*] Director of Research, U. S. Steel Corporation.

fore is operating under conditions approaching those corresponding to equilibrium. For the rate of reduction depends upon how far the $CO:CO_2$ ratio, in the gas layers in immediate contact with the ore particles, differs from the value of this ratio in equilibrium with iron and iron oxide at the particular temperature; and if this ratio is in fact already close to the equilibrium value (which is unaffected by change in total gas pressure), the effect of increased pressure would be relatively small. The precise gain in rate and in economy could be ascertained only by extended trial in a furnace, preferably one now operating at a low coke rate.

R. P. HEUER,* Philadelphia, Pa.—The activity of oxygen in the hearth of the furnace is dependent upon the partial pressure of CO prevailing in the hearth. Consider the reaction

$$C + \tfrac{1}{2}O_2 \rightharpoonup CO$$

$$-\Delta F_0 = RT \ln \frac{A_{CO}}{A_C \cdot A^{\frac{1}{2}}_{O_2}}$$
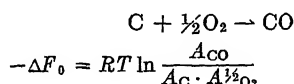
where
$$\Delta F_0 = \text{Free energy change}$$
$$R = \text{Gas constant}$$
$$T = \text{Temperature (absolute scale)}$$
$$A_{CO} = \text{Activity of CO}$$
$$A_C = \text{Activity of C}$$
$$A_{O_2} = \text{Activity of oxygen}$$
$$\ln = \text{Logarithm to base } e$$

For simplification A_C can be made unity, A_{CO} will approximate the partial pressure of CO, whereupon at a given temperature

$$\left(\frac{P_{CO}}{A^{\frac{1}{2}}_{O_2}}\right) = K$$
$$P_{CO} = \text{pressure of CO}$$
$$K = \text{constant}$$

Thus, as the pressure of CO in the hearth rises the square root of the oxygen activity rises proportionally.

In the furnace hearth numerous reactions take place which are influenced at equilibrium by the oxygen activity:

$$MnO \rightharpoonup Mn + \tfrac{1}{2}O_2$$
$$SiO_2 \rightharpoonup Si + O_2$$
$$CaO + \tfrac{1}{2}S_2 \rightharpoonup CaS + \tfrac{1}{2}O_2$$
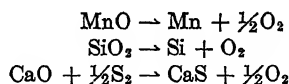
A rise in the oxygen activity would shift the equilibrium of these reactions to the left. Thus the reduction of MnO, SiO_2 and the removal of sulphur from the iron would be affected. For a change in operating conditions that would double the pressure of CO in the hearth without changing the slag composition, the equilibrium would be changed to yield in the resultant iron one-half as much manganese, one-fourth as much silicon and twice as much sulphur as formerly obtained.

T. L. JOSEPH,† Minneapolis, Minn.—At 800° to 1000° C., CO_2 oxidizes C to CO ($CO_2 + 2CO.$). Higher pressures inhibit this reaction or shift the equilibrium to the left. In other words, an increase in pressure inhibits solution loss but promotes carbon deposition. What will happen if carbon is deposited on the exterior of fine Mesabi

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* Vice President in Charge of Research, General Refractories Co.
† Professor of Metallurgy, Minnesota School of Mines and Metallurgy.

ore particles, or in the space between the lumps where room is needed for the gas to pass? In other words, will mechanical difficulties arise? The original work in Germany showed that higher pressures increased carbon deposition. If carbon deposition increases with higher pressures, gas flow will be restricted because only about 8 to 10 per cent of the volume in the furnace is effective as space for movement of the gas. There is considerable interstitial space in the charge through which the gas does not move freely. If carbon deposition is increased it might have a detrimental effect.

In Europe they seem to think that carbon deposition is desirable, and with coarse ores that might be true. If the problem is to reduce the center of a coarse lump, carbon deposition in the center of that piece might be desirable. But with the Mesabi ores the problem is to get the gas to the surface of the ore. The particles are small, and require little time to reduce. Most of the ore particles are smaller than ¼ inch.

This whole problem is, however, extremely interesting, and I thoroughly agree that it would be a fine thing to test on a commercial scale. Pressure operation appears to have possibilities, but the only way we can determine its practicability is to actually try it out.

J. M. AVERY.—Professor Joseph has raised an interesting point, and one to which I have given considerable thought.

Replying first to Dr. Johnston, what I hope can be accomplished with pressure operation is to force the reduction of iron ore to take place in such low-temperature zones, i.e., higher levels in the furnace, that solution loss can be greatly decreased and in many cases practically eliminated. Dr. Austin's assumptions* differ from actual furnace operation in a very important respect. In the furnace we do not have a closed system where FeO and other oxides of iron ore are maintained at a constant assumed temperature, but rather a counter-current flow of both gases and ore, so that in actual fact, and as revealed by a number of analyses of ores taken out of the furnace at various levels, considerable iron is reduced to the metallic state fairly high in the furnace. Consequently, these calculated equilibria may check pretty well with a good many furnaces blown at as high a blast rate as furnaces are now blown and, therefore, Dr. Austin's assumptions may seem to be correct. Nevertheless, I am quite certain that the assumptions will not hold good under pressure operation where reduction can be driven to higher levels in the furnace and consequently, lower temperature zones, with the result that a higher ratio of CO_2 over CO, or a lower ratio of CO_2 over CO, becomes possible at equilibrium.

It may thus be feasible to go from CO over CO_2 in the ratio of 2 or 3 to 1 down to less than 2:1; as for example, down to 1.4, which is the lowest value I have seen reported, or even down to 1:1. This may be possible; at least it is not impossible, depending upon the temperature conditions. The change in concentration of CO over CO_2, i.e., the lower ratio of CO over CO_2, is the result of the reduction being completed at lower temperatures, to drive this reaction in the direction to prevent carbon deposition, which I think is the answer to Professor Joseph's question.

There is only one way to find out what the relative importance of these various factors would be in an actual blast furnace, and that is to try pressure operation. It is certainly true that the more effectively the carbon monoxide is used in the lower zones of the furnace, the less strongly will this deposition of carbon tend to occur, other conditions being equal.

I have calculated the amount of carbon deposition on a number of furnaces. Apparently it is seldom extreme. As everyone knows, it occurs only near the top of the furnace where the temperature is low. I am not much afraid of that in pressure reduction, for the reasons stated, and, as Professor Joseph has said, from the stand-

* See page 74, this volume.

point of heat conservation in the furnace, and the effective use of CO, that reaction is desirable.   The only limiting factor would be the plugging up of the interstices of the charge with carbon, or the plugging up of the ore itself with carbon to prevent the gas from permeating it.

Referring to Mr. Heuer's remarks on desulphurization: I am certain that if the absorption of heat in the bosh of the furnace by the solution-loss reaction can be substantially decreased, the net result will be a raising in the level of the melting zone. That means that the metal and the slag will have an opportunity to trickle down through a deeper bed of coke than with furnaces blown hard enough to have a high solution loss.   I would assume that such a change would have a decidedly favorable effect on desulphurization.   It would also tend to increase the silica and carbon, and between those two factors we would have to determine the best blast temperature and, if the gas enrichment is used, at what temperature the enriching gas should be introduced, and the amount of such gas, and so forth.

I believe pressure operation offers a means of exercising far more control over the furnace than has ever before been possible.   It will permit control over both temperatures and reducing conditions in the different zones of the furnace.   You may say that pressure operation is too complicated, but if it means a substantial saving in the cost of producing pig iron, I do not think anything is too complicated.   We will have to come to it.

E. W. DAVIS,* Minneapolis, Minn.—I understand that this has never been tried out on a blast furnace.

G. B. WATERHOUSE,† Cambridge, Mass.—Not yet.   Not so high as Mr. Avery has in mind.

E. W. DAVIS.—And the idea seems to be that if it is tried out, it should be tried out on a bad furnace.

G. B. WATERHOUSE.—That was just a suggestion of Dr. Johnston's, I think.

C. HART, Media, Pa.—I want to speak of carbon deposition.   I started in the iron business about the same time the Mesabi ore first came down.   We had a great deal of trouble with the building of scaffolds and slipping of the furnace, and we attributed it to carbon deposition.   I think that would be the result from a practical standpoint, if the carbon deposition became very pronounced.

J. M. AVERY (written discussion).—Subsequent to the New York meeting, the underlying theory of several aspects of pressure operation was presented in an informal discussion at the Buffalo meeting, in April.   This discussion went into much more detail than was possible or seemed advisable in the original paper, and it was supported by several lantern slides.   As a result of this meeting, the theory of pressure operation seems now to be generally accepted, but on the other hand, as Dr. Johnston suggested, the actual comparative merits of pressure operation can probably be determined only by actual trial.

One question that has been raised frequently is this: If Dr. Austin's theory of coke efficiency is correct, and 1600 lb. per ton of pig-iron capacity approximates chemical equilibrium, how is it possible for pressure operation to bring about a drastic decrease in coke consumption?   The answer to this question is in part given on page 113.   It is perhaps only necessary to remark here that coke consumption as low as 1400 lb. has been reported in actual commercial practice.   As a matter of fact, Dr. Austin himself

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* Superintendent, Mines Experiment Station, University of Minnesota.
† Professor of Metallurgy, Massachusetts Institute of Technology.

remarked that coke consumption as low as 1460 lb. had been reported, but at the expense of pig-iron capacity. It seems clear that Dr. Austin has set up a bogey relating to the normal operation of furnaces, which, as shown in my paper, means that it relates to furnaces that from the standpoint of coke efficiency may be regarded as definitely overblown. That this is so is confirmed by experience with slow blowing, as reported by F. M. Rich and others, and also by the recorded low consumption of coke obtained in various instances. Because of its effect upon solution loss and the profound resulting change in thermal balance within the blast furnace, pressure operation should provide a means for maintaining or even increasing production corresponding to the overblown condition, while at the same time it should be possible to attain coke efficiencies corresponding to consumption at least as low as 1400 lb. per ton of pig iron.

Benefits from the Use of High-iron Concentrates in a Blast Furnace

By C. E. Agnew*

THE Eastern district, composed of New Jersey and eastern Pennsylvania, with its native ores, was the cradle of the iron industry of the United States. The district attained and held the leadership in production of pig iron for over 100 years, from pre-Revolutionary days to approximately 1875. The first shipment of Lake hematite ore was made in 1853. It was a small shipment, transported by a sailing vessel and a canal barge, but it was the beginning of the end of the supremacy of the Eastern district, although at that time the ore was supposed to be too rich to be successfully smelted with the block coal then in use at western furnaces.

The iron made from the first shipment of Lake ore was worked into nails by the Sharon Iron Co., at Sharon, Pa.

The writer's great-grandfather, David Agnew, and his brother, John P. Agnew, owners and operators of the Sharpsville furnace, Sharpsville, Pa., worked the shipment through a furnace. Because of this, the writer feels some satisfaction in having been one of a group that solved the problem of making profitable an operation using Eastern district ores exclusively.

With the development of Lake mines, and the production and use of coke, the Middle West district gradually assumed the position of leadership in production; because, even though the ores were transported 1000 miles by water and rail, its cost figure on pig iron was better than that of the eastern producer whose furnace was next to his mine. Such a cost figure was possible because the ore was naturally rich in iron and reduced easily. It was possible to carry a heavy burden on the furnace, which resulted in large tonnage and low coke per ton of iron.

This paper is in no sense a technical one. The purpose is to show that with the proper physical preparation of the Eastern magnetites they will reduce as easily as the Lake hematites, and because of the high iron concentration give the Eastern producer just as much advantage as formerly he was at a disadvantage in comparison with the Middle West producer.

Indirect and Direct Reduction

In the blast furnace there is indirect and direct reduction of the iron oxide of the ore. The indirect reduction is the action of the gas on the ore as the gas passes up through the stock column. The direct reduction is the final reduction, which takes place at the tuyere zone. Obviously, the greater the percentage of reduction that can be obtained indirectly, the less there will be to do directly; and the less there is to do directly, the greater the possible ore burden—with resulting economies.

It is indirect reduction that for so many years has made the Middle West hematite operation profitable and the Eastern magnetite operation unprofitable. The ease with which an ore lends itself to indirect reduction is due more to a physical property than to a chemical one—and that property is fineness. N. J. Klarding,[1] in a paper read before a meeting of the Iron and Steel Institute, which is described as "the result of an investigation carried out in an apparatus of special design," deals with the formation of the various combinations of Fe and CO. The paragraph of greatest interest to our subject is: "The differences in the heats of formation of various iron oxides are insignificant so far as the reduction is concerned; the $CO:CO_2$ ratio in the gas phase over the oxide, however, is of the greatest importance." The more intimate the contact between the ore and the gas, the greater will be the percentage of indirect reduction and the lower will be the ratio of $CO:CO_2$.

The Lake hematites naturally are soft and earthy in their physical structure, therefore they cannot avoid the contact with the furnace gases so long as the stock distribution is even, as it should be. The voids between the particles of ore are so small the gas must spread out and consequently come into intimate contact with the ore. Fines are objectionable only when they become excessive and cause pressure troubles, with the resulting hanging, slipping and flue-dust losses.

Compare this with any Eastern magnetite in its natural state as formerly charged into the furnace. The ore is hard and refractory. A stock column would be open, with large voids between the ore particles, which would permit the gas to pass through the stock column so rapidly that it could not remain in contact with the ore long enough to have any more than a slight reducing action.

The ratio of surface to mass in the natural hematite is very great, while the ratio of surface to mass in the natural magnetite is very small.

Until recently, Eastern magnetites have been benefited by medium concentration and sintering. This made their use possible but still not particularly profitable when compared with Lake hematites. Various

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[1] N. J. Klarding: Behavior of Iron Ore during Reduction. *Blast Furnace and Steel Plant* (Dec. 1937).

percentages of this sinter were used on furnaces together with Lake or foreign hematites. In most tests, fine hematites were sintered with the magnetites. However, beneficiation of magnetites in the East is now carried to a much higher grade, and extremely high-iron sinter with low silica content has entirely reversed the situation.

PRACTICE AT SCRUB OAKS AND WASHINGTON MINE

In 1930 the Alan Wood Steel Co. acquired the Scrub Oaks and Washington mines, with the expectation of eliminating the Lake and foreign hematites. After many difficulties, this end was attained.

Scrub Oaks ore naturally runs about 30 per cent Fe and 45 to 55 per cent SiO_2. The first operation of Scrub Oaks mine under Alan Wood management gave a concentrate of 12 per cent SiO_2 and 59 per cent Fe. The sinter made from this concentrate was extremely hard and refractory. Even the sintering of the ore was difficult, it being necessary to cut the speed of the sintering machine 50 per cent from the speed normally carried with the hematite-magnetite mixture.

The furnace worked on subnormal pressure, usually about 10 lb., and with a very high top heat, usually about 700° to 800°. A great deal of trouble was experienced with fume in the gas, at times to such an extent that it was necessary to shut down the furnace and clean the gas burners on the stoves and boilers. The coke per ton of iron was prohibitive; basic, approximately 1900 to 2000, and foundry, 2400 to 2500 lb. per ton of iron.

From the existing conditions it was recognized that indirect reduction was not taking place, leaving all the reduction for the high temperature of the furnace bosh. Daily spot gas samples showed a $CO:CO_2$ ratio between 4:1 and 5:1. Various expedients were used in an effort to tighten up the stock column and by so doing force the gas and sinter into contact.

One method was to charge small coke. For a time, 35 per cent of range coke (sized plus ½ in. and minus ¾ in.), from the domestic coke-screening station, was charged. The results were beneficial but not a satisfactory solution.

In an effort to make a more friable sinter, limestone grit was added to the sinter mix. The results were not satisfactory because of the difficulty in controlling the lime percentage due to the build-up of lime in the return fines.

The best results were obtained by screening the sinter to three sizes, minus 1 in., plus 1 in. and minus 2 in., and plus 2 in., then filling in layers of fine, medium and lump. The results obtained were phenomenal in the reduction of coke per ton of iron as well as general furnace operation, but still they were not what is today considered good furnace practice.

The formation of silicates of iron in the sintering process was suspected, as silicates of iron are reduced by CO with difficulty, if at all.

Chemical analysis told nothing, but microscopic analysis showed that silicates of iron were formed in sintering, chiefly in the form of fayalite (Fe_2SiO_4). Under the microscope the percentage of silicates can be determined and, more important still, the manner of their formation. Under the microscope the crystal of iron ore could be seen surrounded by a coating of fused silicate, which prevented the furnace gas from coming in contact with the iron ore and so greatly interfered with indirect reduction.

Obviously, the thing to do was to eliminate the silicate, which could only be done by materially reducing the amount of silica in the ore. Scrub Oaks concentrates now analyze approximately 4.5 per cent SiO_2 and 67.5 per cent Fe. The sinter from this concentrate is quite friable, as against the extremely hard sinter of the higher silica concentrate.

This new concentrate and sinter has been in use two years, with gratifying results. One furnace, newly lined, has produced basic for the past year on an average of 1479 lb. of coke per ton of iron, with a best month of 1379 lb. per ton of iron. This includes the blow-in month. For the year an average of 93 lb. of flue dust per ton of iron has been produced, with a best month of 40 lb. Another furnace, even though in the fifth year of the lining, produced basic on 1500 lb. and 3 per cent silicon iron on approximately 2000 lb. of coke per ton of iron.

The furnace burden is normally 80 to 85 per cent sinter, the remainder being miscellaneous materials such as roll scale, heating cinder, open-hearth slag, etc. For a time, 95 per cent of sinter was used.

Furnace pressures are normal; top heat 350° to 400°. No water is used on the stock. The $CO:CO_2$ ratio runs 2:1 to 2.1:1.

Recently a gradually increasing percentage of raw concentrate has been used. At present 20 per cent of raw Scrub Oaks concentrate (which passes an 8-mesh sieve) is being charged. With this high percentage of fines in the mix, some higher pressures have resulted and it has been necessary at times to check the furnace, but this is not surprising with the heavy total burden ratio of 3.15:1 to 3.25:1. Pressure is the only thing that will stop the use of a greater quantity of raw concentrate.

Conclusions

These facts have been given to show the importance of having a material that will lend itself to the indirect reduction of the furnace gases. From this experience the important new thing learned was of the formation of silicates in sintering Eastern magnetites and the advanced application of microscopic evaluation. For this application we are indebted to Mr. V. H. Lawrence, metallurgical engineer with the Alan Wood Steel Company.

It does not follow that all siliceous ores would form fayalite if sintered. Fayalite forms at a temperature of 2350° to 2800°, depending on con-

tamination, and any ore that sinters at a temperature lower than that would not form fayalite. Of the several magnetites sintered by Alan Wood Steel Co. during the past 10 years, the siliceous Scrub Oaks concentrates was by far the hardest to sinter, because of the fayalite formation. With the lessening of the silica content the same ore made a friable sinter. A high-iron, low-silica concentrate gives:

1. A material that reduces as easily as a Lake hematite, and for the same reason; because it has a large ratio of surface to mass.

2. A material that sinters easily. The sintering itself has nothing to do with the reduction, being simply a means of preparing a fine material for furnace use.

3. A material that contains a small percentage of gangue, thus giving the operator a better control of slag volume. Any necessary silica can be added to the furnace mix in the form of silica rock, which is a by-product of the mine.

4. A material, either raw or sintered, that will not absorb moisture. All moisture is surface only, seldom over 2.5 per cent in the sinter and 5 per cent in the concentrate. The first action under the furnace bell is to drive off moisture from the stock, and the less there is to drive off the sooner the ore can absorb the necessary heat to bring it to the temperature where the CO in the gas can start indirect reduction. Compared to the 12 to 14 per cent of the average Lake hematite, the high-iron sinter and concentrate have the effect of increasing the working volume of the furnace.

5. A material that even in the smallest particle sizes is still granular, as against the very flocculent fines of the Lake hematites, which when dry tend to make flue dust.

DISCUSSION*

(Harrison Souder presiding)

MEMBER.—How is the concentrating accomplished whereby you have reduced the silica so materially in your ore?

R. E. CROCKETT,† Dover, N. J.—I will answer for Mr. Agnew. The Scrub Oak ore contains both magnetite and martite. The concentrating was done by wet magnetic means and also by graphic means, using the jigging table to recover the nonmagnetic units.

MEMBER.—How intimately are the silica and the iron in combination?

R. E. CROCKETT.—The minus 8 mesh is supposed to make a magnetite of much lower concentration, say about 60 per cent. . It is free of martite. That is the first stage of crushing. We rough out a magnetic concentrate and separate from it the

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* See also page 69.
† Superintendent, Alan Wood Steel Co.

silica and the martite, which go together. The silica and the martite are not crushed further but are concentrated after classification by jigging and tabling. The rough magnetic concentrate is then further concentrated.

A. H. FOSDICK,* Bethlehem, Pa.—The Bethlehem Steel Co. owns a magnetite ore body running 40 to 45 per cent iron, as high as 3 per cent sulphur and 0.2 per cent copper. In order to use this ore economically in the blast furnace, it is necessary first to grind and concentrate and then sinter the concentrates. By grinding and concentrating to a material passing through 10 mesh, the iron content has been raised to 58 per cent dry basis, and the sulphur decreased to 0.75 to 1.5 per cent. By further grinding to 65 mesh, the iron content has been brought up to 62 per cent and the sulphur reduced to 0.75 to 1.00 per cent. These concentrates form the basis of the sinter charge for a Dwight-Lloyd plant, which was put in operation in 1930, and for a Greenawalt plant that has been in operation for 20 years.

In 1933 the Bureau of Mines ran a number of experiments on 13 different sinters sent in by as many manufacturers, the results of which were presented in a paper by T. L. Joseph.[2] It was interesting to see that the reducibility rate of those sinters was inversely proportional to the combined FeO plus SiO_2 in the sinter, the one having the least amount of the combined FeO plus SiO_2 being the most easily reduced.

In 1930 our metallurgical department, in conjunction with Professor Turner, of Lehigh University, ran a mineralogical and microscopic investigation on 150 samples of sinter submitted by us. One of the conclusions reached was that in a rapidly cooled sinter much magnetite is entrapped within large iron silicate grains, thus leaving less surface exposed for reduction in the blast-furnace operation.

We are operating four furnaces at Bethlehem at the present time on a very reduced rate of driving. One of these furnaces has a burden of 100 per cent sinter and the other three have 90 per cent. The furnace with 100 per cent sinter has been producing iron on 1500 lb. of coke consistently, with a sinter containing only 57 per cent Fe, with a fluxing stone running from 4 to 6 per cent SiO_2 and with coke containing 11.5 per cent ash and 1.20 per cent S.

Such a rare combination at 67 per cent Fe burden, 1 per cent SiO_2 stone, and coke containing 6.75 per cent ash and 0.7 S, is almost ideal.

Our greatest improvement was a result of the crushing, screening and sizing of coke, obtaining a stone running from 4 to 6 per cent SiO_2 instead of variations from 6 to 15 per cent, enabling us to run a balanced slag ratio of from 0.95 to 1.00 base to acid ratio and higher blast heats.

A blast furnace is much like the human body; its digestive organs are very easily upset. If I had to choose between uniformly bad material and material that is good one day and bad the next, I should take the uniformly bad material, because that would at least give a basis for balancing the furnace.

One feature that we as well as Alan Wood have to take into consideration is that of transportation. It costs just as much to transport silica and moisture units as to transport iron units, which is just one more argument in favor of high-grade raw materials when they can be obtained.

E. SAMPSON,† Princeton, N. J.—May I ask the mineralogical question as to the effect of reduction of silica in the concentrate? Was the silica present in the concentrate as quartz, or as potash feldspar, or both, and was there any relative change

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* Superintendent, Blast Furnaces and Sintering Plant, Bethlehem plant, of Bethlehem Steel Co.

[2] T. L. Joseph: Composition, Physical Properties and Deoxidation of Iron Oxide Sinters. *Blast Furnace and Steel Plant* (March–June, 1933).

† Geologist, Princeton University.

in the proportion of the two when they were reduced? Or, to put it another way, what effect would the potash feldspar, rather than the quartz, have upon the behavior in the furnace?

R. E. CROCKETT.—The silica was present mostly in the form of quartz, although there were some illuminates present. The ratio of the quartz to the illuminates is about 10 to 1 in the crude, and about 10 to 1 in the concentrate.

E. SAMPSON.—And further concentration did not change that ratio?

R. E. CROCKETT.—It seems to me when we reach the critical point, around 68 per cent, the silica is being dropped faster than the illuminates. The illuminate is more intimately mixed with the iron than the silica is. The ore is acidic. If it occurs in an acidic granite, it is hard.

A. H. FOSDICK.—How high a percentage of coke did you have to use in the sinter mix?

C. E. AGNEW.—That depends upon the mixture. We run around 6 per cent carbon. But the higher it goes, the more fuel is diffused, so when we are using 20 or 25 per cent, our carbon will only be about 4 per cent in sintering.

C. R. HAYWARD,* Cambridge, Mass.—Those of us who know what happened to the lead industry when sintering became common, and those who know what has happened since by the making of very much improved sinters, have felt that perhaps the iron-ore industry has something to learn from the nonferrous industry, and I think we can frankly say that the nonferrous industry has very much to learn from the iron industry.

I should like to see this discussion enlarged a little, to include the whole feature of sintering iron-ore fines. Perhaps that is all settled, but it has seemed to me that in any blast furnace to get capacity it is necessary to burn plenty of coke. To burn plenty of coke you need plenty of air, and to have plenty of air you must have an open charge. That certainly leads directly to sintering.

It has seemed to me that even with the Lake ores there is altogether too much fine material put into the furnace. The blast-furnace industry has plenty of flue dust, which has been a curse. This flue dust is high in coke, and certainly could furnish a substantial part of the fuel for sintering.

This paper has interested me from several standpoints. First, because they sinter at all; secondly, because the author points out that by careful experiment and study the sinter has been improved. Obviously, the question of silica and the formation of iron silicate is important because the charge must be kept open, and also in a condition that will permit the reducing gases to do their work in the shaft.

I think we have brains enough in the metallurgical industry to sinter fine iron ores, whether they are Lake Superior ores or magnetites, so that we can get better conditions in the blast furnace.

I sympathize with Mr. Fosdick in wanting uniformity, even if it is poor, but certainly we do not want uniformity with poor charges if we can get them with good charges.

I am merely asking this as a question from my ignorance as a nonferrous metallurgist. Is there not something in the idea that we shall stop putting fine material into the iron blast furnace, and by a happy combination of materials make our charge coarse iron ores and sinter?

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* Associate Professor of Metallurgy, Massachusetts Institute of Technology.

C. E. AGNEW.—In my opinion, fines, so long as they do not give pressure and make flue dust, which is loss, are not objectionable, because the finer the ore is, the more intimate the contact can be with the gas.

We have been doing more experimenting with the use of raw concentrate. I am not going to say now how far we will go, because I do not know. It may be that the sinter will be able to stay in suspension in those gases better than the fine ore.

Since the first of this month, I have had 27 per cent of raw concentrate in the burden, but we are on 75 per cent of blast now. If we were on full blast we probably could not use that amount of fines.

I have worked at Middle West furnaces, and I know their problems. I believe more attention should be paid to the physical preparation of Lake ores rather than to so many engineering features to work the ores as they are.

C. R. HAYWARD.—It is true that if the fine ores will stay in suspension and not cause slips and flue dust, good reduction will follow, but we never get this combination. It seems to me that the iron blast-furnace man has depended more on pressure to get gas through, thus making more flue dust, than he has depended on actual volume. Pressure and volume are not always synonymous. It is only within recent years that this fact has received the attention that it should receive. We want volume, not necessarily pressure, and with an open charge of sinter and coarse ores we can get volume without excessive pressure, which will cut flue dust and improve operating conditions.

C. E. AGNEW.—I mentioned in the paper that our fines, even in the finest particle sizes, are granular as contrasted with the flocculent fines of the Lake hematites. They are the fines that will give more flue dust.

You mentioned lots of coke and lots of air. It takes a certain amount of heat to reduce iron, and a pound of coke will deliver only so many B.t.u. Any additional head that can be obtained from the hot blast will save coke. I have given good figures here, but if we were driving that furnace I could not get the heat I am getting now. I have an 18-ft. furnace blowing 75 per cent capacity, with the result that the air passes through the stove slowly, and I am carrying 1550° on the line, but if I were blowing at full blast, I could not carry more than 1350° or 1400° on the line, and that would change my figures. That proves the point that heat units are what we are interested in; in other words, with the same furnace, if I were to increase the wind, and could back it up with heat, I would make the same coke and larger tonnage.

A. H. FOSDICK.—May I try to answer Professor Hayward? I think his thoughts are along the right line. Our Lackawanna plant uses Lake ore. It was producing as much as 500 lb. of flue dust per ton of pig, which anybody will agree is pretty high. The American Ore Reclamation Co. owns the Buffalo sintering plant, adjacent to our Lackawanna plant. About seven years ago we joined forces with them in this way: We screened out the fines from our beaver ore, which is a Mesabi ore, and put about 25 to 40 per cent of the beaver fines in the sinter. The Buffalo company was attempting to sinter nothing but flue dust. I do not know what Mr. Linney's reaction is, he has done much work along that line and is one of the deans of sintering, but my thought is that nobody ever succeeded in sintering flue dust alone. The Buffalo sintering plant was transformed into a paying proposition, a good sinter was produced, the fines were taken out of the Lake ore at Buffalo, the flue-dust losses were cut from 500 to 80 lb. and the coke rate improved accordingly.

O. LEE,* Birmingham, Ala.—We all know that many of the iron ores, particularly those running from 10 per cent and up in silica, will form some fayalite during the

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* Metallurgist, Republic Steel Corporation.

sintering operation. Since we must add limestone as a fluxing agent in the blast furnace, what would be the effect upon fayalite formation of adding the limestone to the sintering charge?

C. E. AGNEW.—The difficulty is in controlling the lime. We tried that twice, at different times. At first it would work pretty well but in the course of time the return fines would build up the lime percentage and the irregular feed would result in spotty sinter.

I understand the thought back of your question. One of the purposes of trying the lime was to try to form a simple silicate before the iron silicate formed, but it did not work. But the greatest objection from the furnace man's viewpoint is that the sintering becomes unmanageable. There were a couple of days during which we did not put any stone at all into the furnace, just working off the lime sinter. We found above 5 per cent; the lime would not fuse into the sinter at all. It was just a physical mixture.

C. P. LINVILLE,* Bound Brook, N. J.—One interesting point with regard to this sintering is that about 200 lb. of the equivalent of coke is used in making the sinter for one ton of iron, and the coke is reduced in the furnace, but the coke is still being used in preparing the material. However, I suppose that coke screens in the present day are considered to be worthless.

C. E. AGNEW.—For the carbon of the sinter mix we use anthracite culm. I like the culm; I think it mixes a little more intimately. Any carbon that might be in the flue dirt is all carbon, but, to quote Mr. Joseph, that carbon in the flue dirt deteriorates, and stock flue dirt loses two-thirds of its efficiency. But if used directly, it is all right. If you get flue dirt it is an advantage to cut that carbon, because you make a better quality of sinter.

C. P. LINVILLE.—That is because the ordinary flue dirt has so much carbon in it for the job it has to do. If you only want 5 per cent carbon and there is 8 per cent in the flue dirt, it would be well to add something to it. The carbon in the flue dirt, of course costs nothing, but my point is that we are making iron in some furnaces for 1400 lb. of coke, or the carbon in 1400 lb. of coke, but we must remember that we are putting 200 lb. more in the sinter in order to make the sinter.

C. E. AGNEW.—That carbon is gone when it gets to the furnace; it is burned. That would come into the cost of the sinter. It has no effect so far as the reduction of the iron in the furnace is concerned. The fact remains that it is necessary to use carbon to put the ore into proper condition for use in the furnace.

Passing to the other point, the reason for not sintering—that is, charging as much raw concentrate to the furnace as possible, to avoid the sintering cost. The cost is approximately 60¢ a ton to sinter, and if 20 per cent of raw ore can be added to the furnace that much has been saved in sintering cost.

R. A. LINDGREN,† East Chicago, Ill.—It seems to me that this problem of sintering ores has got to be worked out as to the economies for each individual plant. I am afraid that the impression might be gained here that those of us who work on Lake ores and do not sinter them are all out of order.

Mr. Fosdick pointed out that there are certain Lake ores that must be sintered whereas other ores work well in the blast furnace without sintering. We had an illustration of that. One of the ores we brought down was a form that tended toward a limonitic structure. When we put that ore in the furnace burden the flue dust per

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* Metallurgist, The Calco Chemical Co.

† Superintendent, Blast-furnace Dept., Wisconsin Steel Works, International Harvester Co.

ton of iron increased in the neighborhood of 300 or 400 lb. over and above normal. We installed a sintering plant and sintered that ore, and we were able to use it with normal dust loss. Of course, the ideal situation, as Mr. Fosdick pointed out, obtains if the sintering plant can be brought down to the furnaces, and then the fines screened out and sintered with the flue dust. It is not necessary to add the carbon that is required when sintering only ore.

Mr. Agnew speaks of the low coke rate. Have any carbon balances been worked out in regard to the Alan Wood practice to show how much direct and how much indirect reduction the furnaces are working on?

C. E. AGNEW.—No, we have not done that.

R. A. LINDGREN.—It might be interesting to try it. You might be surprised.

W. R. Cox,* New York, N. Y.—I am reminded by Mr. Agnew's paper of certain blast-furnace tests made in 1922–1923, with the furnace burden consisting of a large percentage of a high-grade beneficiated product. It was not a sinter, but the coke consumption was reduced to around 1350 lb. per ton of pig iron produced. The blast pressure was reduced from around 14 to 15 lb. to as low as 12½ lb. The production of pig iron per day was increased from around 450 tons to 650 to 700 tons; the hours between checks to as high as 54, with many other improved operating conditions. So that it would seem there is nothing new under the sun, this has all been done, and it is a sign of progress to have the consumers wake up to the fact.

P. E. HENRY,† Paris, France (written discussion).—The methods resorted to at Scrub Oaks do not apply to the lean Lake ores, the valorization of which is the most important problem confronting the iron-ore industry of the United States.

Iron-ore beneficiation research follows entirely different ways in Europe and in the States. In the States they try to throw the whole burden of valorizing the lean ores on their beneficiation previous to their use in the blast furnace. The ideal would be to obtain practically pure iron oxide, well sintered and to make from it a high-quality pig iron with a very low coke consumption. In Europe they are gradually coming to the opposite point of view. The blast furnace itself is more and more considered primarily as a concentrator. Pig iron, whatever its quality, is in fact a very high-grade concentrate. The idea is to obtain from the blast furnace any metal at all with a high iron recovery at the lowest possible cost, and then to refine this metal in order to turn it into either foundry iron or steel of usual specification. The problem is to reduce and melt the iron ore with the smallest possible amount of slag at the lowest possible temperature. No attention is paid to the amounts of sulphur, phosphorus, silicon, carbon or other impurities. Their elimination belongs to the refining part of the process.

Some rather astonishing results have been obtained lately in this direction. Large-scale tests made at Roechling's have shown conclusively that the south German dogger iron ore, containing as mined only 19 per cent iron, can be turned into raw pig iron with a coke consumption as low as 1050 kg. (2352 lb.) per 1000 kg. (2205 lb.) of raw pig iron. Of course this coke consumption may sound very high to American steel people, who aim at a consumption of only 750 kg. (1658 lb.) of coke. (By the way I should like to know whether in Agnew's paper a coke consumption of 1500 lb. per ton of iron means per ton of 2000 lb. or per ton of 2240 lb. When shall you do away with what Lord Kelvin called a wickedly brain-destroying piece of bondage?) But it should be remembered that every kind of beneficiation, even sintering, is

* Consulting Engineer.
† Consulting Mining Engineer.

dispensed with, and the corresponding saving should be put against the extra coke consumption.

As to the refining of the raw pig iron thus obtained, it is known now that carbonate of soda can deal with sulphur at a low cost. Increased attention is also being paid to the Ugine-Perrin processes. Perrin has shown that almost any raw metal can be brought very quickly to almost any desired composition by putting it in intimate contact with a properly chosen liquid slag.

Of course each trend has its limitations. It has been known for years, long before Alan Wood entered the field, that low-grade magnetites can be concentrated and sintered at a profit. The Scrub Oaks showing is in no way better than the results obtained long ago at Syd Varanger starting from 30 to 32 per cent siliceous magnetite. The Syd Varanger briquettes are known in Europe as the very best ore that exists. They are 66 to 68 per cent iron and so porous that air can be blown with the mouth through them. Iron recovery is well over 90 per cent. But thus far it seems fairly well established that previous beneficiation of the ore does not apply economically to any other type of iron ore than magnetite. Here is the field of the opposite trend, which turns the blast furnace into a concentrator able to deal efficiently with almost any rubbish containing some iron.

R. H. SWEETSER.—The ton of pig iron in Mr. Agnew's paper is 2240 lb.

Relative Desulphurizing Powers of Blast-furnace Slags, II

By W. F. Holbrook*

In a previous paper[1] a method for the measurement of the comparative desulphurizing power of slags was described and data were presented covering the range of likely slags containing up to 10 per cent MgO. In the present work the range is extended to include slags containing up to 20 per cent MgO, and the effect of temperature on 5 per cent and 15 per cent MgO slags over the range 1475° to 1525° C. is included. The method used was that described in the previous paper except that some of the temperature measurements were made with a noble-metal thermocouple instead of a tungsten-graphite thermocouple. Twelve-gram charges of 0.8 per cent sulphur-metal and 5-gram charges of slag were subjected to heating for 30 min. at a prescribed temperature. The charges were analyzed for sulphur content. For purposes of comparison, desulphurizing power is defined as the ratio of the percentage of sulphur found in the slag to that found in the metal. Six slag and metal charges were made coincidentally in ⅝-in. holes in a section of an electrode graphite rod. One slag and metal charge was used as a control by means of which adjustment in the desulphurization value could be made for small variations in temperature and other factors. For convenient presentation of the data, the slags are arranged in groups in each of which one of the four main slag components is constant. Thus, the 15 per cent MgO slags are presented separately from those containing 20 per cent MgO.

SLAGS WITH MAGNESIUM OXIDE CONSTANT

15 *Per cent MgO.*—The data on slags containing 15 per cent MgO cover a composition range of 24 to 50 per cent SiO_2, 5 to 27 per cent Al_2O_3 and 24 to 53 per cent CaO. Variation in composition has been in steps of 2 per cent over much of the area. Because the change in desulphurization power is generally gradual with gradual change in composition, certain sections have been covered in steps of 4 per cent and even

more.   Table 1 shows the desulphurization values obtained using slags of the several compositions indicated, and Fig. 1 gives the same data graphically.   Each curve passes through all points representing slags of a given relative desulphurizing power.   Actual values found differ occasionally from the values indicated by the curves on account of experimental error, but the slope of the curves as indicated by several experimental points is unmistakable.   The 15 per cent MgO slags were not found to be greatly different in their desulphurizing character from 10 per cent MgO slags.   The slopes of the isodesulphurization lines are similar over much of the composition area.   That is, any given small change in composition in a 15 per cent MgO slag will affect its desulphurizing power
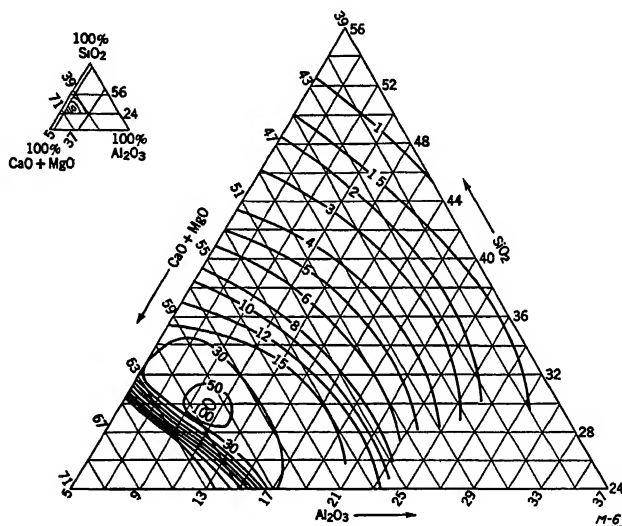
Fig. 1.—Composition-desulphurization diagram of 15 per cent MgO slags a 1500° C.

in much the same way as would a corresponding change in a similar 10 per cent MgO slag.   The diagram shows that, in general, desulphurization is affected less by a substitution of Al_2O_3 for SiO_2 and conversely than by substitutions involving CaO and Al_2O_3 or CaO and SiO_2.   It also shows that at 1500° C. the optimum composition contains about 60 per cent of total bases (CaO + MgO), slightly more than in slags with less MgO.   Furthermore, the maximum value obtained with 15 per cent MgO was 110, considerably greater than the 84 obtained in the 10 per cent MgO series.   Desulphurization increased steadily and rapidly as composition was changed toward the more basic, until the optimum was reached.   Further increase in basicity caused a rapid decrease in desulphurizing power, which accompanies a rapid increase in viscosity.

20 *Per cent MgO.*—Slags containing 20 per cent MgO are shown in Table 2 and Fig. 2.   They differ from the 15 per cent MgO slags mainly

in that the area of optimum composition for desulphurization has been shifted toward the higher basicity and lower Al_2O_3 section of the diagram.

TABLE 1.—*Comparative Desulphurizing Power of* 15 *Per Cent MgO Slags at* 1500° C.

Composition, Per Cent							
SiO_2	Al_2O_3	CaO	R^a	SiO_2	Al_2O_3	CaO	R^a
50	7	28	1.3	34	10	41	21.0
50	11	24	0.6	34	12	39	13.0
				34	14	37	9.8
48	5	32	2.3	34	16	35	6.7
				34	23	28	2.5
46	11	28	1.6	34	27	24	1.0
46	15	24	0.8				
				32	6	47	38.0
44	6	35	3.5	32	8	45	37.0
44	9	32	3.0	32	10	43	34.0
				32	12	41	18.0
42	6	37	4.1	32	14	39	12.0
42	8	35	3.8	32	16	37	10.0
42	15	28	2.1	32	18	35	6.3
42	19	24	1.1	32	21	32	5.2
40	6	39	7.7	30	6	49	3.0
40	8	37	5.5	30	8	47	45.0
40	10	35	4.2	30	10	45	110.0
40	13	32	4.1	30	12	43	35.0
				30	14	41	32.0
38	6	41	10.4	30	16	39	19.0
38	8	39	7.7	30	18	37	12.0
38	10	37	6.6	30	20	35	8.1
38	12	35	5.0	30	27	28	1.7
38	19	28	2.9				
38	23	24	1.4	28	7	50	0.3
				28	9	48	1.4
36	6	43	13.0	28	11	46	11.1
36	8	41	11.0	28	13	44	33.0
36	10	39	10.5	28	15	42	31.0
36	12	37	6.6				
36	14	35	5.1	25	7	53	1.9
36	17	32	5.2	25	11	49	2.4
				25	15	45	43.0
34	6	45	24.0	25	19	41	27.0
34	8	43	40.0	25	23	37	12.0

$$ {}^a \quad \frac{\text{Per cent S in slag}}{\text{Per cent S in metal}} $$

The maximum desulphurization value obtained was only 55. Heretofore it has been found that as the MgO was raised the optimum basicity

increased and the maximum desulphurization value observed also increased.   In the 20 per cent MgO series of slags that trend seems therefore to have changed.   The change is shown by Table 3.

TABLE 2.—*Comparative Desulphurizing Power of 20 Per Cent MgO Slags at 1500° C.*

Composition, Per Cent							
SiO_2	Al_2O_3	CaO	R^a	SiO_2	Al_2O_3	CaO	R^a
52	5	23	0.8	34	9	37	19.0
52	9	19	0.5	34	11	35	14.0
				34	13	33	8.9
48	5	27	2.0	34	17	29	4.6
48	9	23	1.3				
48	13	19	0.7	32	5	43	55.0
				32	7	41	46.0
44	5	31	4.8	32	9	39	37.0
44	9	27	2.3	32	11	37	28.0
44	13	23	1.4	32	13	35	19.0
44	17	19	0.9	32	17	31	6.0
				32	21	27	3.1
42	5	33	6.4	32	25	23	1.3
42	9	29	3.6				
				30	5	45	6.6
40	5	35	9.6	30	7	43	47.0
40	9	31	5.2	30	9	41	25.0
40	13	27	2.5	30	11	39	16.0
40	17	23	1.8	30	13	37	20.0
40	21	19	1.0	30	15	35	17.0
				30	17	33	9.0
38	5	37	14.0	30	21	29	5.6
38	7	35	10.0				
38	9	33	7.0	28	7	45	2.0
38	13	29	4.9	28	9	43	11.7
				28	11	41	18.0
36	5	39	27.0	28	13	39	21.0
36	7	37	13.0	28	15	37	17.0
36	9	35	9.2				
36	13	31	6.0	25	7	48	0.35
36	17	27	3.0	25	11	44	1.6
36	21	23	1.5	25	15	40.	12.0
36	25	19	0.9	25	19	36	9.5
				25	23	32	4.4
34	5	41	33.0				
34	7	39	27.0				

$$^a\ \frac{Per\ cent\ S\ in\ slag}{Per\ cent\ S\ in\ metal}$$

TABLE 3.—*Effect of MgO Content on Desulphurization Value of Optimum Composition*

MgO, Per Cent	Optimum Total, Bases (CaO + MgO)	Maximum Desulphurization Value
0	52	14
5	55	23
10	58	84
15	60	110
20	63	55

TEMPERATURE

In making the studies on desulphurization, a temperature of 1500° C. has been taken as one of the standard conditions. This temperature is within the range commonly observed in blast-furnace operation, but
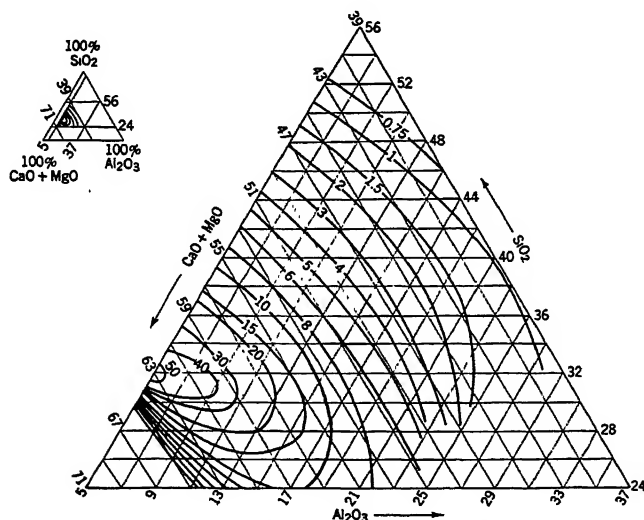
FIG. 2.—COMPOSITION-DESULPHURIZATION DIAGRAM OF 20 PER CENT MgO SLAGS AT 1500° C.

other temperatures do obtain and a knowledge of the effect of temperature on desulphurization by slags is desirable. A systematic survey was made at two temperatures other than 1500°; namely, 1475° and 1525° C.

Owing to the uniformity of the results obtained in the 1500° tests and the fact that the variation of desulphurization with composition change was gradual, it was thought to be unnecessary to cover the composition areas in as great detail as before. Therefore, temperature tests were made on 5 per cent and 15 per cent MgO slags only, with the other components changing in steps of 4 per cent and in some cases 5 and 6 per cent. Tables 4 and 5 and Figs. 3 and 4 give the results obtained with

5 per cent MgO slags. The two diagrams present very much the same appearance; the difference lies mainly in the values represented by the isodesulphurization lines. It is of interest to note that the ratio between
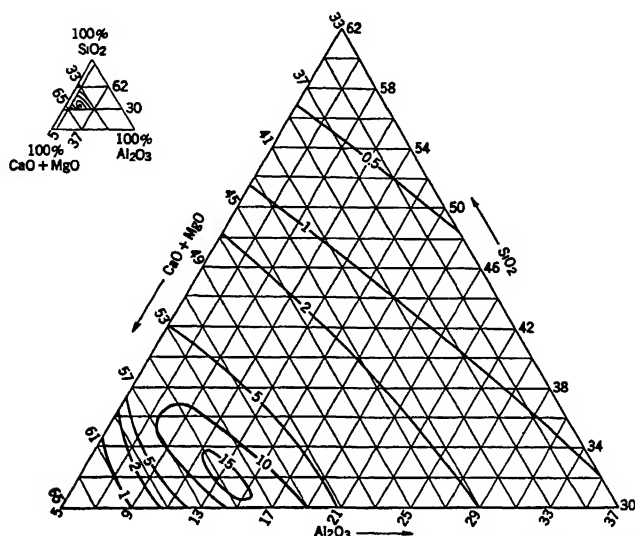
FIG. 3.—COMPOSITION-DESULPHURIZATION DIAGRAM OF 5 PER CENT MgO SLAGS AT 1475° C.
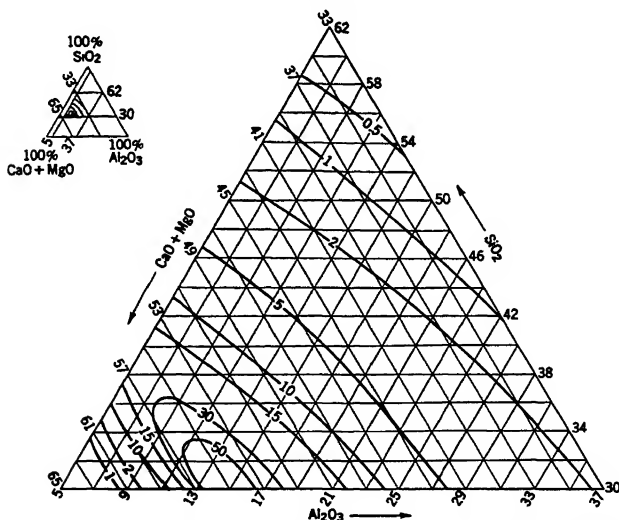
FIG. 4.—COMPOSITION-DESULPHURIZATION DIAGRAM OF 5 PER CENT MgO SLAGS AT 1525° C.

the desulphurizing power of many of the slags at 1525° to the desulphurizing power of the same slags at 1475° is about 2 to 1. Another difference between the two diagrams is in the position of the areas of optimum

composition. Raising the temperature, like increasing the MgO content, shifts the area of optimum desulphurization toward the high CaO corner of the diagram. It is significant that both of these factors result in a

TABLE 4.—*Comparative Desulphurizing Power of 5 Per Cent MgO Slags at 1475° C.*

Composition, Per Cent			
SiO_2	Al_2O_3	CaO	R^a
54	6	35	0.6
54	10	31	0.5
50	6	39	1.1
48	12	35	0.9
48	16	31	0.6
46	6	43	3.2
44	12	39	1.9
42	6	47	4.5
42	10	43	3.4
42	18	35	1.3
42	22	31	0.8
38	6	51	9.2
38	14	43	3.3
38	18	39	2.6
36	12	47	7.0
36	24	35	1.6
36	28	31	1.1
34	6	55	1.4
34	10	51	14.0
34	18	43	3.1
32	8	55	1.6
32	24	39	3.1
30	10	55	1.9
30	14	51	9.2
30	18	47	12.0
30	22	43	3.9
30	30	35	1.8
30	34	31	1.3

[a] $\dfrac{\text{Per cent S in slag}}{\text{Per cent S in metal}}$

TABLE 5.—*Comparative Desulphurizing Power of 5 Per Cent MgO Slags at 1525° C.*

Composition, Per Cent			
SiO$_2$	Al$_2$O$_3$	CaO	R^a
54	6	35	1.2
54	10	31	0.9
54	14	27	0.4
50	6	39	2.2
48	12	35	1.7
48	16	31	1.0
48	20	27	0.7
46	6	43	5.0
44	12	39	3.6
42	6	47	12.0
42	10	43	7.1
42	18	35	2.6
42	22	31	1.5
42	26	27	0.9
38	6	51	24.0
38	14	43	7.2
38	18	39	5.0
36	12	47	16.0
36	24	35	3.4
36	28	31	2.3
36	32	27	1.3
34	10	51	48.0
34	18	43	12.0
32	24	39	6.2
30	10	55	2.8
30	14	51	94.0
30	18	47	30.0
30	22	43	15.0
30	30	35	4.2
30	34	31	3.2
30	38	27	1.7

a $\dfrac{\text{Per cent S in slag}}{\text{Per cent S in metal}}$

decrease in the viscosity of the highly basic slags.   Raising the temperature or increasing the MgO content of the slag, or both, appears to make possible the use of slags of higher basicity.

TABLE 6.—*Comparative Desulphurizing Power of 15 Per Cent MgO Slags at 1475° C.*

Composition, Per Cent			
SiO_2	Al_2O_3	CaO	R^a
54	5	26	0.7
50	5	30	1.2
50	9	26	0.6
46	5	34	2.7
46	9	30	1.6
46	13	26	0.9
42	5	38	4.9
42	9	34	2.5
42	13	30	2.0
42	17	26	1.1
38	5	42	9.7
38	9	38	5.6
38	13	34	3.8
38	17	30	2.2
38	21	26	1.3
36	5	44	19.0
34	5	46	7.8
34	7	44	28.0
34	9	42	15.0
34	13	38	7.4
34	17	34	3.9
34	21	30	2.3
34	25	26	1.2
32	7	46	1.2
32	9	44	56.0
30	9	46	1.1
30	11	44	71.0
30	13	42	27.0
30	17	38	10.0
30	21	34	4.4
30	25	30	2.3

$$a\ \frac{\text{Per cent S in slag}}{\text{Per cent S in metal}}$$

The 15 per cent MgO slags are affected by temperature changes in much the same way, as is shown by Tables 6 and 7 and Figs. 5 and 6. Here, again, the isodesulphurization contours present a similar appearance, the difference in desulphurizing values of a given slag is about 2 to 1 at the two temperatures, 1525° and 1475° C., and the higher temperature shifts the optimum area toward the high CaO corner of the diagram.

TABLE 7.—*Comparative Desulphurizing Power of 15 Per Cent MgO Slags at 1525° C.*

Composition, Per Cent							
SiO_2	Al_2O_3	CaO	R^a	SiO_2	Al_2O_3	CaO	R^a
58	5	22	0.4	36	5	44	37.0
54	5	26	1.0	34	5	46	114.0
54	9	22	0.7	34	7	44	48.0
				34	9	42	37.0
50	5	30	2.5	34	13	38	18.0
50	9	26	1.1	34	17	34	8.6
50	13	22	0.8	34	21	30	5.2
				34	25	26	3.5
46	5	34	5.5	34	29	22	1.7
46	9	30	4.3				
46	13	26	1.8	32	5	48	111.0
46	17	22	1.2	32	7	46	465.0
				32	9	44	77.0
42	5	38	9.4				
42	9	34	6.7	30	5	50	1.9
42	13	30	4.3	30	7	48	320.0
42	17	26	2.9	30	9	46	128.0
42	21	22	1.3	30	11	44	89.0
				30	13	42	54.0
38	5	42	20.0	30	17	38	22.0
38	9	38	11.0	30	21	34	11.0
38	13	34	6.8	30	25	30	5.2
38	17	30	5.0	30	29	26	2.9
38	21	26	3.2	30	33	22	1.1
38	25	22	1.6				

a $\dfrac{\text{Per cent S in slag}}{\text{Per cent S in metal}}$

As pointed out in the earlier paper, a temperature rise results in an increase in the desulphurizing power of all slags, but the increase is greatest toward the area of viscous, highly basic slags. Except in these slags, the effect of temperature change seems to be uniform.

The temperature range, 1475° to 1525° C., covered in this study is probably less than might be desired. The consistency of the data and

the similarity in the slope of the curves at the two temperatures, however, will justify some degree of extrapolation beyond these limits.
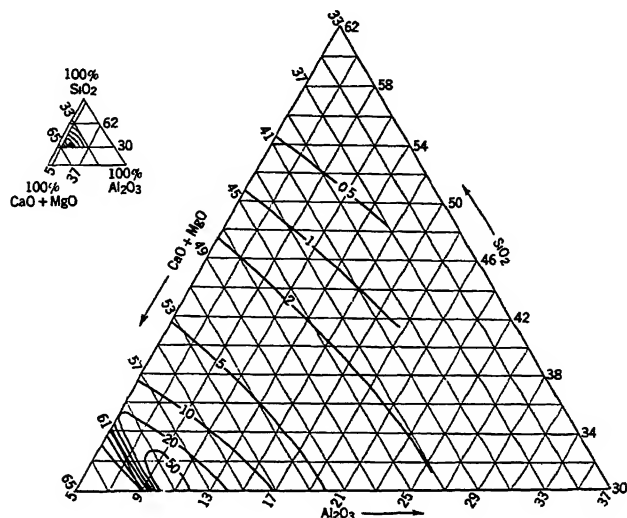
FIG. 5.—COMPOSITION-DESULPHURIZATION DIAGRAM OF 15 PER CENT MgO SLAGS AT 1475° C.
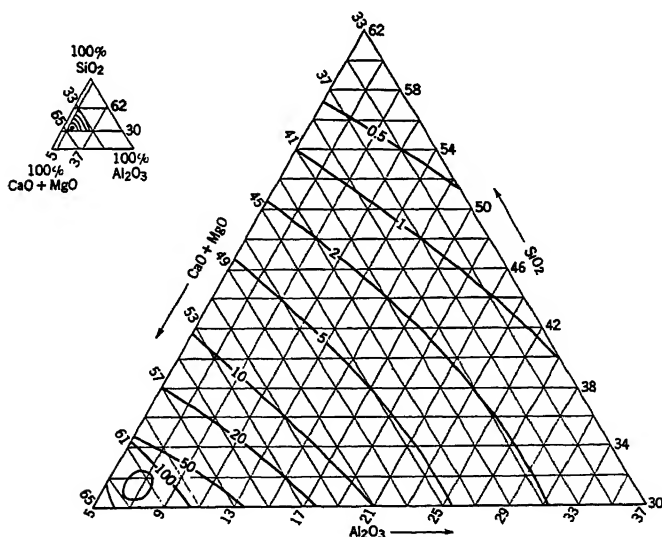
FIG. 6.—COMPOSITION-DESULPHURIZATION DIAGRAM OF 15 PER CENT MgO SLAGS AT 1525° C.

SUMMARY

The data here presented, together with those previously reported, show the comparative desulphurizing character at 1500° C. of practically any possible slag composition within a range of approximately 30 to

50 per cent SiO_2, 5 to 25 per cent Al_2O_3, and 35 to 65 per cent bases (CaO + MgO), and, in addition, scattered compositions outside these ranges.

The generally accepted fact that increased basicity improves desulphurization is corroborated, but the data show that for a given MgO content there is an optimum basicity beyond which the slags become very poor desulphurizers. The isodesulphurization contours show that the composition is critically related to desulphurization at optimum and higher basicities and less so in the range of less basic slags.

In general, the data show that a slight improvement may be expected from the replacement of a small amount of SiO_2 by a like amount of Al_2O_3. Also, small substitutions of MgO for CaO cause slight decreases in desulphurization. Neither of these statements holds true, however, in the areas of optimum composition.

On the other hand, replacement of CaO or MgO by Al_2O_3 or SiO_2 shows comparatively large effects in most of the composition areas.

Increasing the temperature from 1475° to 1525° C. was found to double the desulphurization ratio of most of the ordinary blast-furnace slag compositions.

The magnitude of the change in desulphurizing power that may be expected from any given change in the composition of a slag or from any limited change in temperature is shown by diagrams (Figs. 1 to 6).

DISCUSSION
(George B. Waterhouse presiding)

C. HART, Media, Pa.—In the year 1900 I was told that there was no compound of magnesia and sulphur known, like the sulphide of lime. I have asked about that for the past 37 years and invariably have received the answer "No."

T. L. JOSEPH,* Minneapolis, Minn.—You asked that question last year.

C. HART.—And did not get an answer.

T. L. JOSEPH.—When we returned to Minneapolis, we fused some magnesium silicate and held the slag over high-sulphur metal. The temperature was necessarily high to get the magnesium silicate sufficiently fluid. Sulphur was removed from the metal with magnesium silicate. In fact, it was slightly more active than calcium silicate. To be somewhat more explicit regarding the formation of MgS, in our experiment we compared the desulphurizing power of silicate slags containing 40 per cent MgO and 40 per cent CaO, respectively. The test was made in the manner described in the paper except that a higher temperature was necessary. The magnesia slag removed sulphur from the metal, leaving only 0.008 per cent. The lime slag allowed 0.038 per cent S to remain under the same conditions. Since sulphur was removed by contact with magnesium silicate, it seems certain that magnesium sulphide was formed. I do not see how the sulphur would otherwise get out of the metal and into the slag.

The proportion by weight of slag and metal was the same and the temperature was controlled. In other words, we tried to isolate the effect of various factors such as temperature and composition.

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* Professor of Metallurgy, Minnesota School of Mines and Metallurgy.

G. B. WATERHOUSE,* Cambridge, Mass.—The whole question of desulphurization is very important, and very much to the point just now.

R. P. HEUER,† Philadelphia, Pa.—I have been making laboratory studies to determine the distribution of sulphur between molten iron and slags of various lime-silica ratios. I have been using special slags of very low viscosity, thereby speeding up the reaction rate to more nearly approach equilibrium. For a considerable range in composition of my slags the logarithm of the ratio of sulphur percentage in the slag to sulphur percentage in the iron is directly proportional to the ratio of lime to silica in the slag.

These slags contained up to 15 per cent of alumina and 3 per cent of magnesia. I am not prepared to speak fully about these experiments at present but can say that it is possible with lime slags to get a ratio of sulphur in the slag to sulphur in the iron as high as 2000:1 or 3000:1 or higher.

J. T. MacKENZIE,‡ Birmingham, Ala.—Using molecular percentages instead of weight percentages, we find in cupola slags that MgO does as much as CaO, and it does not weigh nearly so much. I think the figure might change on recalculation to that basis.

T. L. JOSEPH (written discussion).—The data presented in Mr. Holbrook's present paper and a former one upon which the writer collaborated afford a means of comparing the relative desulphurizing power of blast-furnace slags differing widely in composition. Comparisons of the desulphurizing power of specific slags can be made by locating the composition on the triaxial diagrams and noting the relative desulphurizing powers. Each diagram, however, is limited to slag of constant magnesia content when held at one temperature. From all the triaxial diagrams given in the two papers a variety of curves can be drawn to show the effect of slag basicity, temperature, the replacement of SiO_2 by Al_2O_3, and the replacement of CaO by MgO. For the purpose of summarizing the data on slags falling within the range of practice, a set of curves given in Figs. 7 to 10 was prepared.

In Fig. 7 the CaO plus MgO and the SiO_2 plus Al_2O_3 equal 50 per cent in all cases. The basicity equals unity if we define basicity as

$$\frac{\text{Per cent CaO + per cent MgO}}{\text{Per cent SiO}_2 + \text{per cent Al}_2O_3}$$

This expression for basicity does not afford a good index of relative desulphurizing power because the slags exhibited significant differences in the amount of sulphur removed. If, however, basicity is expressed as

$$\frac{\text{Per cent CaO + per cent MgO}}{\text{Per cent SiO}_2}$$

desulphurization improves with increasing basicity except for magnesia-free slags having a basicity exceeding 1.50. Beyond this range of basicity the slags are too viscous at 2732° F. or 1500° C. to function properly in removing sulphur.

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* Professor of Metallurgy, Massachusetts Institute of Technology.
† Vice President in Charge of Research, General Refractories Co.
‡ Metallurgist and Chief Chemist, American Cast Iron Pipe Co.

Each of the four curves shows the effect of replacing SiO_2 with Al_2O_3 at constant temperature and a constant concentration of magnesia. In the upper curve for magnesia-free slags the CaO is constant at 50 per cent. The Al_2O_3 steadily increases from 6 to 18 per cent while the SiO_2 decreases from 44 to 32 per cent. This substitution of Al_2O_3 for SiO_2 steadily increases the desulphurizing power of the slags and is consistently related to the basicity expressed as the ratio of the total bases to the silica. For comparisons of slags of widely different composition, this ratio appears to offer the best index of desulphurization and accordingly appears to be the most useful manner of expressing basicity.
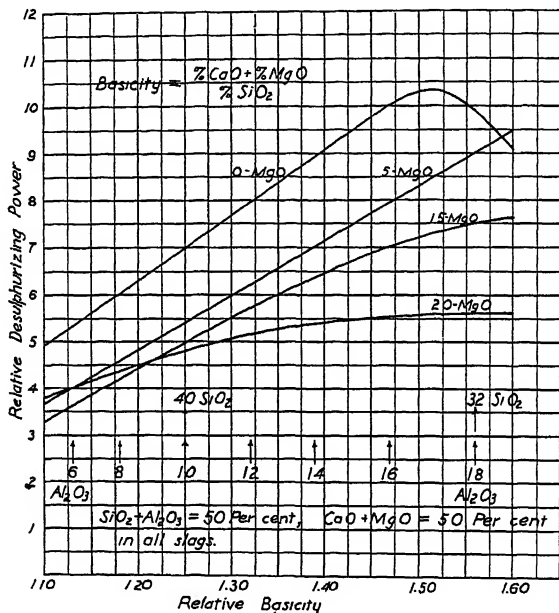
FIG. 7.—EFFECT OF REPLACING SILICA WITH ALUMINA ON DESULPHURIZING POWER OF BLAST-FURNACE SLAGS (2732° F.).

Attention is called to the reversal in the desulphurizing properties of magnesia-free slags when the basicity exceeds 1.50. All the magnesia-bearing slags would show a similar reversal if basicity were increased beyond the limits of practice and the temperature remained constant at 2732° F. Higher temperatures shift this reversal towards more basic slags. Very basic slags are excellent desulphurizing mediums at high temperatures but poor ones at moderate temperatures because of high viscosity.

The position of the four curves shows that slags of higher magnesia content are less efficient in removing sulphur. With 20 per cent magnesia the curve is decidedly flat, showing that magnesia tends to stabilize the desulphurizing power of the slag. As the basicity increases desulphurization does not increase normally.

Fig. 8 shows the effect of magnesia in a somewhat different range of composition. All the slags in this figure contain a constant amount of Al_2O_3 (15 per cent). Since the Al_2O_3 is constant, the slags in this group show the effect of replacing SiO_2 with CaO and MgO. In the normal range of basicity the slags of higher magnesia content are definitely less effective in removing sulphur. For example, if we consider a slag with

36 per cent SiO_2 and a basicity of 1.36, the $CaO + MgO = 49$ per cent. The percentage composition of the magnesia-free slag is: SiO_2, 36.0; Al_2O_3, 15; CaO, 49. This slag has a relative desulphurizing ratio of about 7. If we substitute 20 per cent MgO for 20 per cent CaO and retain the same basicity and the same percentages of SiO_2 and Al_2O_3, the CaO decreases from 49 to 29 per cent and the desulphurizing ratio drops from 7 to 4.5.

These figures cannot be translated into practice but the data show that the substitution of MgO for CaO definitely decreases the desulphurizing action of the slag.
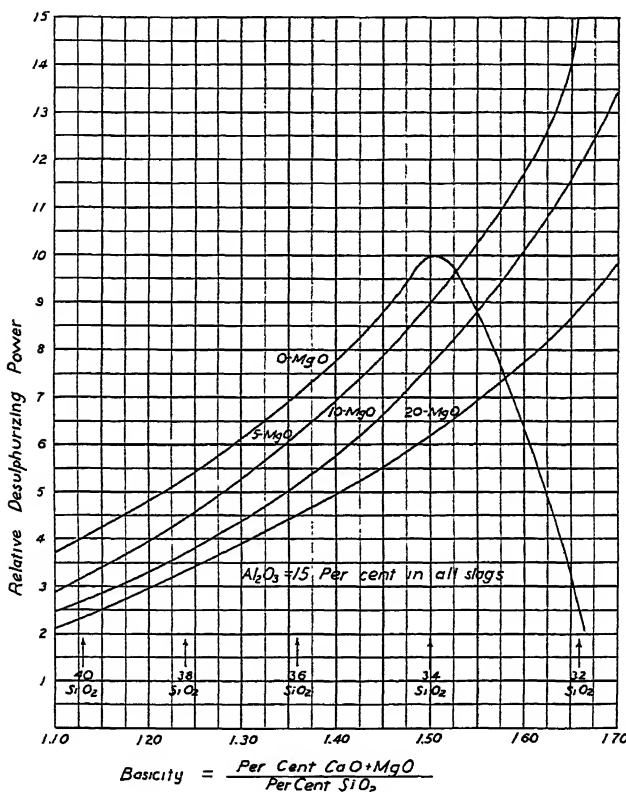
FIG. 8.—EFFECT OF REPLACING LIME WITH MAGNESIA ON DESULPHURIZING POWER OF BLAST-FURNACE SLAG (2732° F.).

If magnesia has any merit in promoting desulphurization, it is in connection with very basic slags beyond the limits of normal practice.

In the laboratory tests made by the Bureau of Mines, the temperature of the metal and the slag were the same. This, of course, is not true in practice, as there is a definite drop in temperature at greater distances below the tuyeres. Fig. 9 shows the effect of temperature on two series of slags, one containing 5 and the other 15 per cent MgO. All the slags contain 14 per cent Al_2O_3, which makes it possible for the interested reader to compute the exact composition of all the slags from the data given in the figure. A comparison of the two groups shows that slags containing 15 per cent MgO do not respond to higher temperatures as readily as the slags containing 5 per cent MgO. The extreme right portion of the 15 per cent MgO series is much lower than a similar

position on the 5 per cent series. Moreover, the curves for the 15 per cent series are much flatter, indicating that the MgO tends to stabilize the desulphurizing power of the slag. Professor McCaffery and his co-workers found that MgO had a similar stabilizing effect upon the viscosity of slag.

In the 5 per cent MgO series, which covers the range of Lake ore practice except for Al_2O_3, the improvement in desulphurization is moderate in the low-temperature range but increases much more sharply at temperatures above about 2730° F. In the acid slags a rise in temperature of 50° F. approximately doubles the desulphurizing
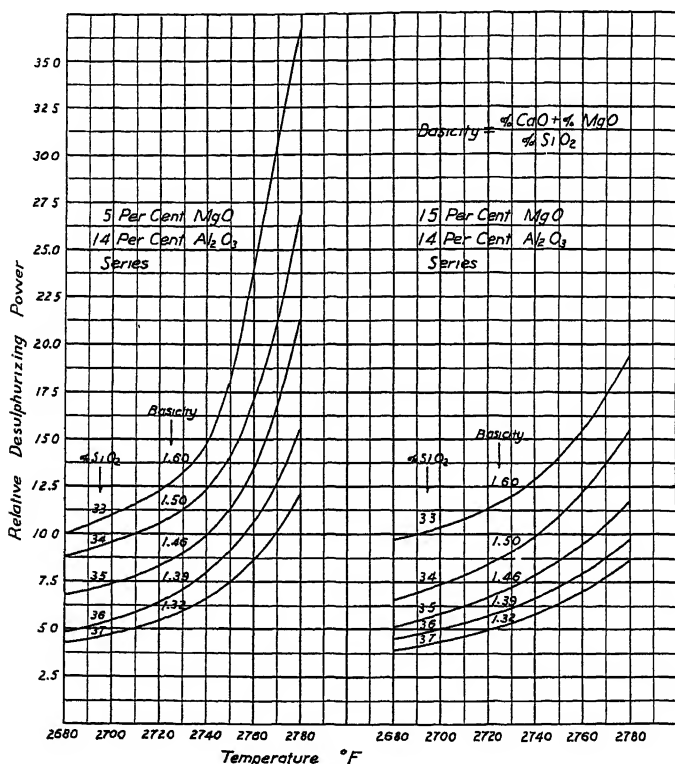
Fig. 9.—Effect of Temperature on Desulphurizing Power of Blast-furnace Slag.

ratios while in the more basic slags this same increase in temperature above 2730° F. approximately trebles the desulphurizing power of the slags.

The upper and lower curves in the 5 per cent series cover the range of basicity in normal practice. At the highest temperature of 2780° F., changes in composition produce the greatest divergence in desulphurizing power. From an acid slag, 37 per cent SiO_2, to a basic slag, 33 per cent SiO_2, the improvement of this rather wide change in composition on desulphurization is about the same as an increase in temperature of 40° F., or about 22° C. The importance of temperature regulating desulphurization is very evident.

The effect of temperature on desulphurization is shown again in Fig. 10. In the series of curves on the left the sum of the bases equals 50 per cent and in the series on the right the bases total 51 per cent. This rather small difference in composition has an appreciable effect on desulphurization in the lower temperature range but it is more

apparent in the high-temperature range. In both series of curves the replacement of SiO_2 by Al_2O_3, which is in effect an increase in basicity, improves the desulphurizing power of the slags. The rather sharp improvement in desulphurization above about 2730° F. as compared to lower temperatures is again apparent.

W. F. HOLBROOK (written discussion).—In his discussion Mr. Joseph has given a practical demonstration of the use of the triaxial diagrams for the comparison of slags in limited ranges of composition. It should be borne in mind that the present paper, together with the previous one upon which Mr. Joseph collaborated, is intended to present desulphurization data on a wide range of slag composition and with a minimum of confusion. These data constitute a survey from which individuals may choose data covering the limited fields in which their interest lies.
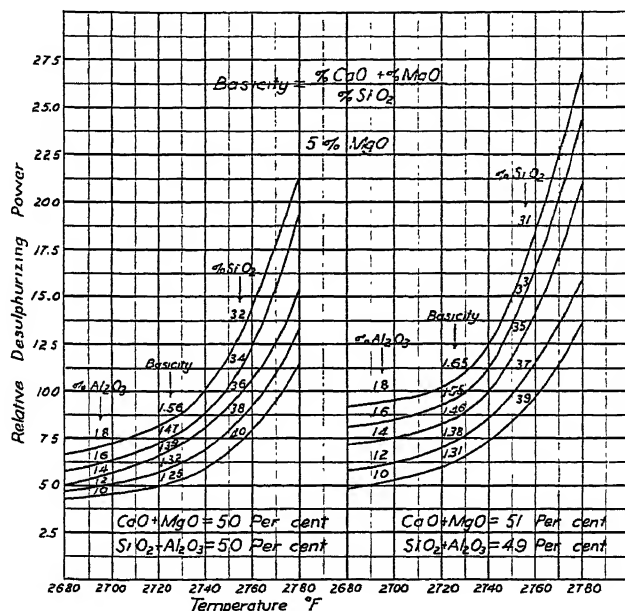
FIG. 10.—EFFECT OF TEMPERATURE ON DESULPHURIZING POWER OF BLAST-FURNACE SLAGS (SiO_2–Al_2O_3 SERIES).

Although in our former paper, in trying to relate desulphurization to basicity, we concluded that "Al_2O_3 cannot be ignored as is frequently done," Mr. Joseph has revived the following formula for the basicity of a slag:

$$\frac{\text{Per cent } CaO + \text{per cent } MgO}{\text{Per cent } SiO_2}$$

Inasmuch as a separate curve is required for each MgO level, the expression might be further simplified, and within certain limits desulphurization would be proportional to the ratio

$$\frac{\text{Per cent } CaO}{\text{Per cent } SiO_2}$$

Such expressions are often practical, but it seems to me cannot be recommended for general use.

The observation made by Mr. Joseph that the temperature drops below the tuyeres and that therefore conditions in practice differ from those obtained in the tests seems to have no bearing on the problem.   Since desulphurization is conceived to occur across an almost vanishingly thin interface, the temperatures of the two phases at any point where the reaction is proceeding must be essentially equal.   Therefore the making of tests in which the slag and metal were at different temperatures would be pointless, even if they were possible.

Mr. Joseph's curves show clearly the nature of the effect of temperature change on desulphurization.   Data were obtained at only three temperatures—namely, 1475°, 1500° and 1525° C. (2687°, 2732° and 2777° F.)—which I felt to be insufficient to justify curves.   Mr. Joseph's curves fill a definite purpose, however, and I am grateful to him for supplying them.   It should be pointed out that each of these curves represents a single slag of definite composition rather than a group of slags of indicated basicity.

Desulphurizing Pig Iron by Ladle Treatment with Soda Ash or Caustic Soda, and a Nontechnical Discussion of the Reactions of Alkali Slags

By George S. Evans*

CERTAIN American operators believe that desulphurizing in the ladle offers a means of increasing blast-furnace and open-hearth yields with the possibility of improvements in quality of the steel. In fact, several producers have experimented with practically all of the known desulphurizing agents, including both standard grades of the alkalies and special preparations that have been offered from time to time during the past several years. Some of these are regularly being used today in large-scale commercial operations, with good results. Also, it is the practice to treat off-sulphur casts in the blast-furnace ladle at a number of plants.

It is not known, however, that anyone in the steel industry (American) has ever adequately equipped a plant for desulphurizing blast-furnace metal in an efficient manner as regular operating practice. The purpose of this paper is to illustrate the importance of correct equipment and proper handling for obtaining uniform and efficient results.

As will be shown, at the temperature of molten iron the alkalies are instantly neutralized by any free slag present, dissipating their desulphurizing value. Entrained silicates are rapidly washed out of the metal bath by the highly basic soda slags and will be satisfied ahead of desulphurizing reactions with FeS. More or less of the reagent will always be used up through reactions with the refractory lining. Desulphurization will be limited to the action of the free alkali then remaining in the slag.

Causes for the erratic results generally found with desulphurizing tests in blast-furnace transfer ladles would include, among other things, variations in the quantity of furnace slag coming down with the metal, and differences in the percentage of kish and entrained silicates in the different casts. As the alkalies instantly unite with any free slags or silicates present, these, with any kish coming off, both dilute the reagent and reduce the surface contact between the slag and metal, thereby retarding the desulphurizing reactions.

Wide variations in tests with desulphurizing between the mixer and open hearth can usually be attributed to variations in amount of kish-slag accumulations in the mixer going out with the pour, rate at which ladles are filled (or extent of agitation by the stream) and time allowed for the reactions.

The foregoing clearly illustrates the impracticability of attempting to desulphurize as a regular practice in the ordinary blast-furnace ladle. However, with the proper equipment and correct handling, uniform desulphurizing can be obtained either between the blast furnace and mixer or between the mixer and open-hearth furnaces.

IMPORTANCE OF EQUIPMENT

Layout for Blast-furnace Open-hearth Operations.—An ideal layout for desulphurizing between the blast furnace and mixer is shown in Fig. 1. This includes a ladle car for holding one complete cast, slag-trap spout ladles for multistage desulphurizing and hoods with exhaust stack for carrying off fumes. This layout, with 30-ton ladles, would handle 3000 tons of molten metal per day. The arrangement provides for more or less complete separation of slag and kish. It also permits of pouring the metal into the desulphurizing ladle slowly, thus prolonging the stirring action of the stream in whipping portions of the refining slag down into the metal bath—two prime essentials to efficient desulphurization.

The special slag-trap spout ladle illustrated by Fig. 2 is equally adaptable for desulphurizing between the mixer and open-hearth furnace. Where it is the practice to transfer iron from the furnace in open-top ladles, this type may sometimes be used to advantage. Slag and kish would be held back by the trap when pouring into a second desulphurizing ladle of this same design. Desulphurizing can be accomplished with ordinary ladles by skimming off the transfer ladle, then slowly pouring the metal into a second ladle to which the reagent has been added and finally skimming off the soda slag. However, the self-skimming ladle will generally produce more efficient results and is much to be preferred.

Uniform Desulphurizing at Low Cost.—By knowing the approximate sulphur content of the metal from the furnace, and varying the treatment accordingly, any specifications down to 0.02 per cent sulphur could be uniformly met, within an approximate range of plus 10 per cent, for widely varying sulphur irons (up to 0.10 per cent). In other words, a 0.07 per cent sulphur iron can be reduced by 50 per cent (0.035 per cent) within the approximate range of 0.032 to 0.039 per cent, or the same iron can be reduced by 70 per cent (to 0.021 per cent) within the range of 0.019 to 0.023 per cent sulphur, whichever is wanted.

With the proper layout the cost of desulphurizing 0.07 per cent iron to 0.035 per cent (50 per cent) and under, including reagent, labor and refractories, should not exceed 30¢ per ton to the Pittsburgh, Chicago, or

Birmingham districts. For reducing the same iron down to 0.021 per cent (70 per cent) and under, the cost would approximate 60¢ per ton or less. Under favorable conditions these cost figures might be reduced by one-half or more.
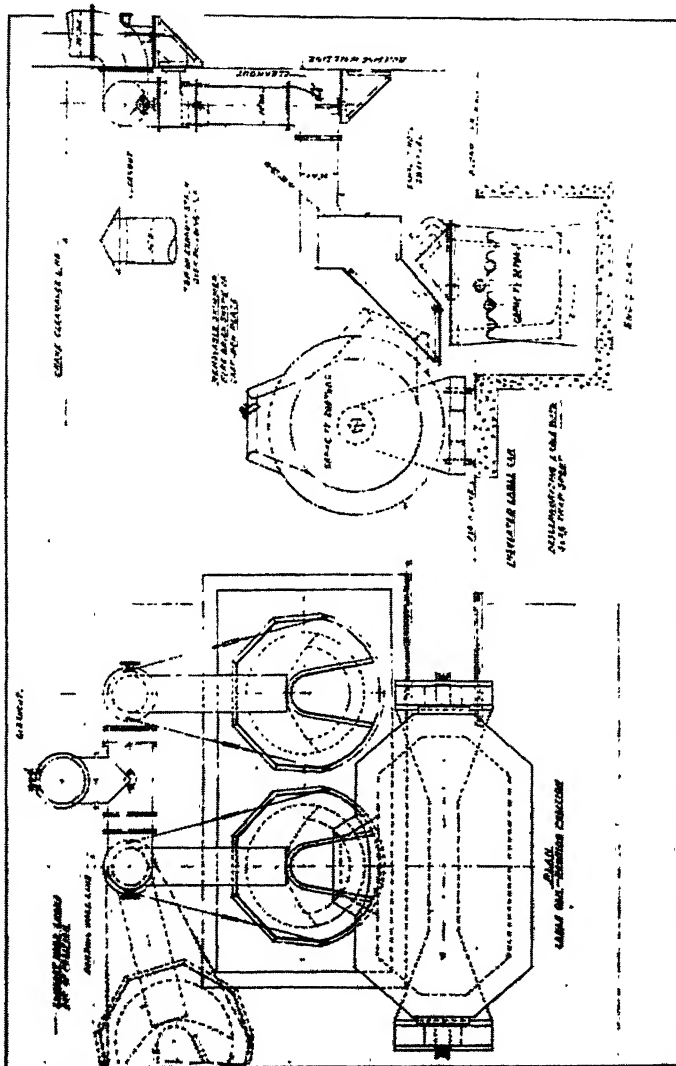
FIG. 1.—DESULPHURIZING LAYOUT RECOMMENDED FOR BLAST-FURNACE OPEN-HEARTH OPERATIONS.

Early Failures Due to Inadequate Equipment.—In the light of past experiences, the foregoing may seem impractical to most or all early experimenters in the steel industry, many of whom have found results so erratic as to discredit the value of desulphurizing in practical steel-mill practice. Early experiments with desulphurizing in the foundry industry

were equally unsatisfactory and for the same reason—inadequate or ill adapted equipment and improper handling. Today, however, a large proportion of the iron castings produced in the United States are desulphurized, or, more appropriately stated, refined with fused soda ash.

Refining Iron for Castings.—Refining in the foundry industry is considered as distinct from desulphurizing in duplexing processes, although the same principles apply. While sulphur reductions of 60 to 80 per cent are regularly being made in the steel industry, experience shows that
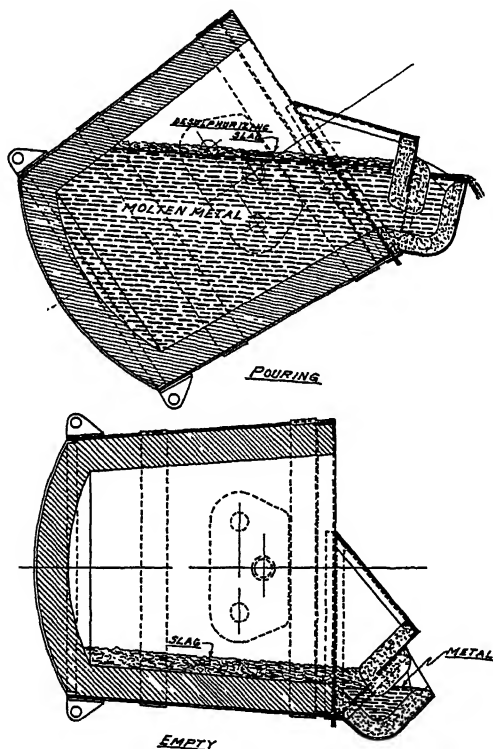
FIG. 2.—DESULPHURIZING LADLE WITH SLAG-TRAP SPOUT.
Top, pouring position; bottom, empty except for slag that is held back by slag trap.

reductions of only 25 to 40 per cent usually give the best results in average foundry practice. In this industry the removal of entrained oxide silicates, which are washed out with the sulphur, plays an equal or even more important part in determining the value of improvements in castability of the molten iron and in the soundness and machinability of the finished castings.

Uniformity of results throughout each cast and from day to day is, however, the prime essential to successful desulphurizing in foundry operations. The extent to which this is obtained is nicely illustrated in

Fig. 3, which shows the log of an 8-hr. heat at a large foundry making cast-iron pipe. Desulphurizing was accomplished with fused soda ash in the special elongated teapot refining ladle, Fig. 4.

Provided with the right equipment and with correct handling, equally uniform results can be expected in steel-mill practice, for any sulphur reductions required in regular operations.

Multistage Process Makes for Uniformity and Saves Reagent.—The slag-trap spout ladle illustrated in Fig. 2 was designed especially for
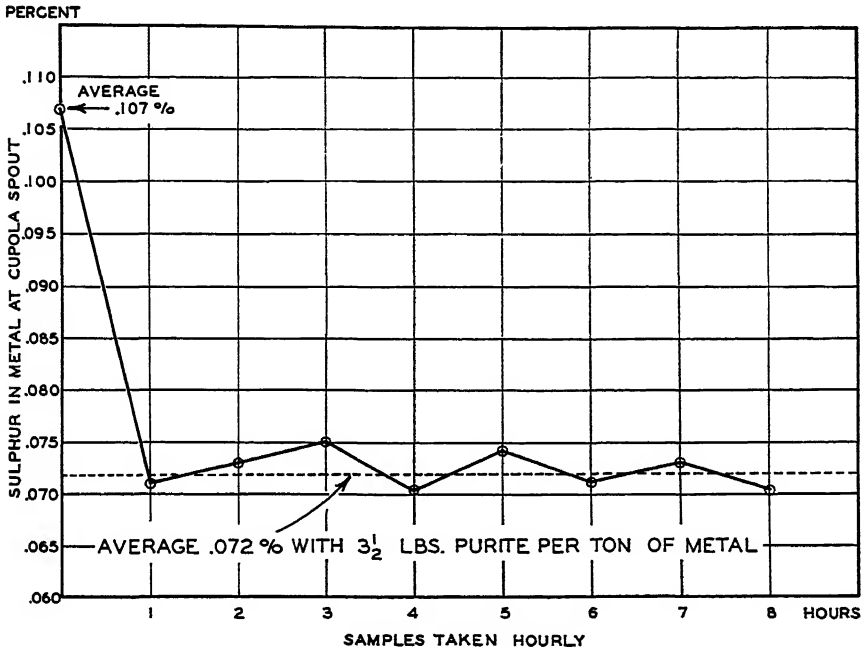
FIG. 3.—SULPHUR REDUCTION WITH PURITE IN NEW ELONGATED TEAPOT LADLE.
The new elongated mixer refining teapot ladles, which are covered and insulated, reduce temperature loss of metal in mixer to a minimum. These ladles also make for maximum desulphurizing efficiency and greater uniformity of analyses and physical properties in finished castings. (Data from eight-heat test run in cast-iron pipe foundry.)

desulphurizing by the multistage process (patented). In this process an excess of reagent is added to the first ladle in order to build a good volume of slag required for maximum desulphurizing efficiency. The partially spent soda slag is held back in the ladle by the slag-trap spout (as shown in Fig. 2), and is revivified by additions of approximately ⅓ the original amount of reagent for treating the second ladle. The same procedure is followed for the third ladle except that still smaller additions of reagent are usually added. In this way a saving of about 50 per cent in reagent is made for a given amount of sulphur reduction, as compared to treatment in ordinary lip ladles and skimming off the slag. Moreover, this process

of re-using the soda slag makes for uniform results—at minimum cost—from ladle to ladle.   This is well illustrated in Table 1.

Refractory, or ladle-lining, maintenance costs, which make up from 10 to 25 per cent of the total cost of desulphurizing, average somewhat more with the slag-trap type of ladle, but this usually is offset many times over by the savings in cost of reagent.

TABLE 1.—*Data Taken from Practical Plant Operations*

Ladle	Sulphur in Iron, Per Cent		Sulphur Reduction, Per Cent	Treatment, Pounds Fused Soda Ash per Net Ton
	Before Treatment	After Treatment		
1	0.105	0.041	61	35
2	0.103	0.034	67	+10
3	0.105	0.042	60	+ 5
Average..........	0.104	0.039	63	16.7

SELECTION OF REAGENT

Alkalies Available for Desulphurizing.—The alkalies available for use in obtaining the lower sulphurs required in American open-hearth practice would include, in the order of their activity: (1) soda ash (Na_2CO_3); (2) soda ash, caustic mixtures; (3) caustic soda (NaOH).   These chemicals are rated in commercial parlance on the basis of their sodium oxide (Na_2O) content—thus caustic soda with 76 per cent Na_2O is more active than soda ash with 58 per cent Na_2O.   Limestone and fluorspar are sometimes added with soda ash for treatment of very high-sulphur irons (0.15 to 0.70 per cent sulphur).

Under favorable conditions, upward of 85 per cent of the sulphur present in molten cast iron (0.06 per cent sulphur or over) can be removed with caustic soda in one treatment without external heat.   The maximum reduction obtainable when treating similar iron with soda ash is about 70 per cent.   The percentage reductions with treatment of lower sulphur irons would be proportionately less, for the reasons indicated in Fig. 5. Owing to its greater activity, however, variations will be somewhat less with caustic soda.   By carrying out the operation in two steps, slightly increased total reductions over the percentages mentioned can sometimes be obtained.

The reagent required for best results would depend somewhat upon the manner of carrying out the operations, but more largely upon the temperature and composition of the metal and the extent of desulphurizing required.   With temperatures of 2550° F. and over, straight soda ash could generally be used for desulphurizing to the extent of 50 or 60 per cent of the sulphur present.   With lower temperatures, and for

uniform reductions of 70 to 80 per cent, mixtures of caustic soda and soda ash (Sulfex) will generally prove more efficient.   On very low-tempera-
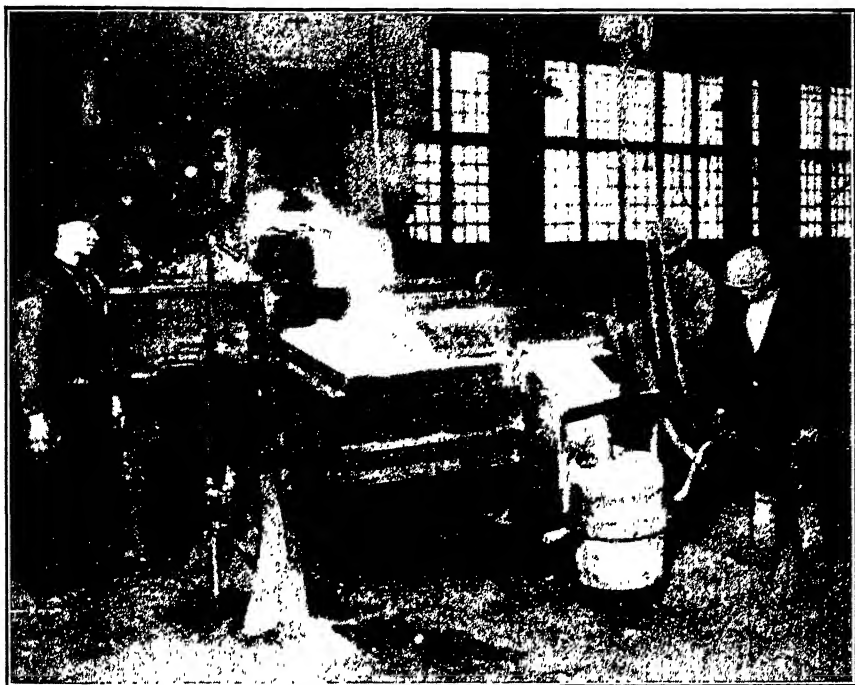
FIG. 4.—NEW ELONGATED TEAPOT MIXER LADLE.
Reagent is added at one end, where stream of iron enters.   Slag travels across ladle and off through slag spout at far end opposite teapot spout.

ture metals, or for obtaining extremely low sulphurs, straight caustic soda might be required.

REACTIONS

Chemical Reactions Involved.—The reactions between the metal and soda slag and within the slag, as with open-hearth slags, are both varied and complicated.   However, from the standpoint of the end results and for the purpose of discussion, these reactions may be expressed by the following simple equations:

$$Na_2CO_3 + SiO_2 \qquad = Na_2SiO_3 + CO_2 \qquad\qquad [1]$$
$$FeS + Na_2CO_3 + 2C = Na_2S + Fe + 3CO \qquad\qquad [2]$$
$$2Na_2S + 3O_2 \qquad = 2Na_2O + 2SO_2 \qquad\qquad [3]$$
$$Na_2S + FeO.SiO_2 \qquad = Na_2SiO_3 + FeS \qquad\qquad [4]$$
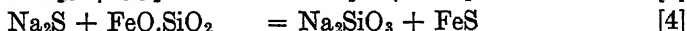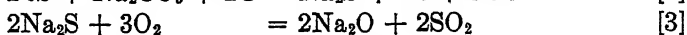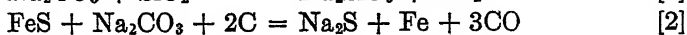
It is assumed in this discussion that the major portion, if not all, of the sulphur in molten pig iron occurs either as iron sulphide (FeS), which is soluble in molten iron, or as manganese sulphide (MnS), an insoluble compound suspended in the metal bath.

Active Reagent Dissipated by Slags and Silicates.—Reaction 1 (Na_2CO_3 to Na_2SiO_3) is taken to represent all combinations between the alkali reagent and free slags or entrained silicates in all molten cast iron. · This equation also represents reactions of sodium with silicon (FeSi) and corrosion of the refractory lining.

These slags and silicates are all acid-to-alkaline soda slags and not only have a greater affinity for the alkalies than sulphur, but their very nature (with the exception of FeSi in solution) make for more rapid and intimate contact with the soda slag. Hence it is obvious that this neutralizing reaction 1 normally proceeds at a faster rate than reaction 2 (FeS to Na_2S), which is assumed to represent the true or principal desulphurizing reaction. The removal of sulphur as MnS, which occurs coincident with and at about the same speed as the reaction with entrained silicates, is considered to be more a mechanical or scrubbing action.

The reactions of sodium with silicates not only occur at relatively faster rates than reactions with FeS, but result in more stable compounds. Once sodium (Na) combines with silicon (Si) in combination with other elements, its value as a desulphurizing agent is lost.

Desulphurizing Reactions.—Reactions 1 and 2, including any reactions with manganese sulphide, may be considered as primary reactions. Reaction 2 is taken to illustrate the true chemical process of desulphurizing. These reactions proceed at widely varying rates, depending upon the quantity and condition of siliceous inclusions or free slag present, and upon the percentage of sulphur in the iron. For instance, with an excess of free slag, such as would come down with the molten pig iron without the use of a skimmer or slag trap in the blast-furnace runner (or when allowing cupola slag to flow out with the metal), the reaction with silicates Na_2CO_3 to Na_2SiO_3 would predominate to the practical exclusion of the desulphurizing reaction FeS to Na_2S.

Again, in the absence of any free slags but in the presence of suspended or entrained oxide silicates, reaction 1 still proceeds at a fast rate until all silicates have been satisfied. From this stage on reaction 1 is limited, except for corrosive action on the refractory lining, to any reactions with dissolved silicon (FeSi), and therefore proceeds at a slower rate, more nearly comparable to reactions with FeS.

Desulphurization Varies with Amount of Sulphur Present.—Under constant conditions, the speed of reaction FeS to Na_2S varies directly with the amount of sulphur present in the metal. Thus for a given treatment the "percentage" sulphur reduction will always tend to remain more nearly constant for all sulphur contents, provided an excess of alkali remains; also the "points" sulphur reduced or weight removed will always be greater with higher than with lower sulphur irons. This will be recognized as being in accordance with the law of mass action.

For instance, it is found in actual practice that 10 lb. of fused soda ash per ton of molten cast iron ($\frac{1}{2}$ of 1 per cent) used under favorable conditions of temperature and composition of metal, will ordinarily reduce sulphur from 0.10 per cent down to about 0.04 per cent (0.06 points) or
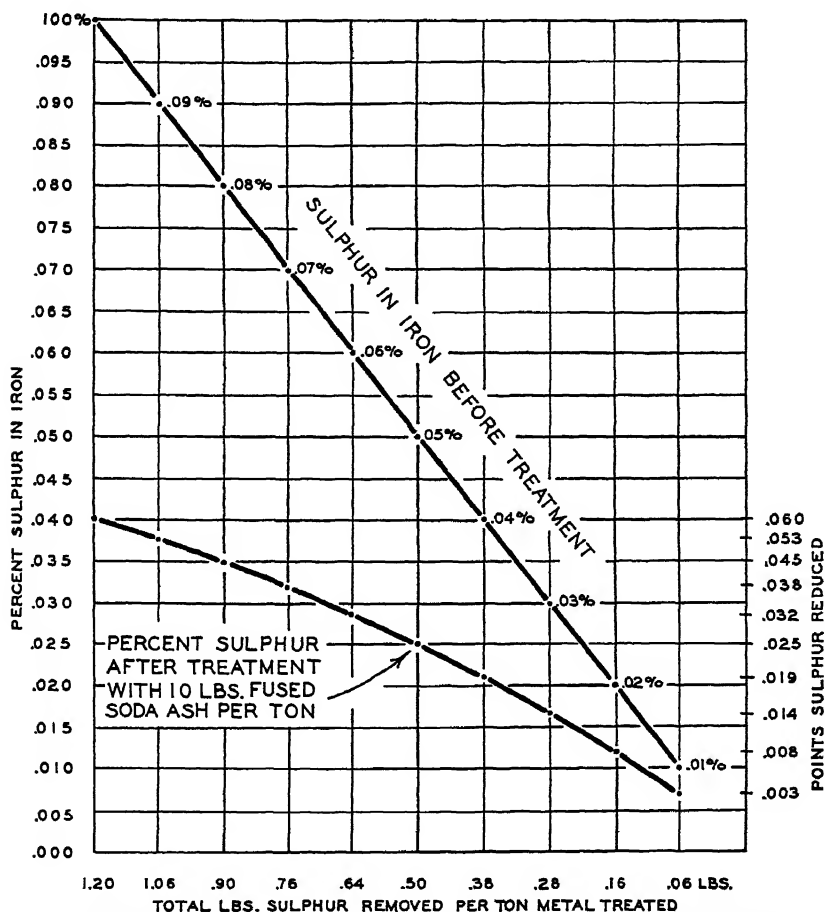
Fig. 5.—Normal sulphur reduction by 10 lb. soda ash per ton of molten iron with varying sulphur contents.

Upper curve represents sulphur contents of molten cast iron, varying from 0.10 to 0.01 per cent sulphur, before treatment.

Lower curve is projected to show approximate percentage reduction and pounds sulphur removed by 10 lb. fused soda ash per ton molten iron. This represents average expectancy with ladle treatment in actual foundry practice.

60 per cent reduction, in one treatment without external heat. The same treatment under similar conditions will reduce an 0.05 per cent sulphur to about 0.025 per cent (0.025 points) or 50 per cent reduction; similarly, 0.025 per cent sulphur is reduced to about 0.015 per cent (0.01 point), or approximately 40 per cent reduction.

This action of soda slags applying in ladle treatment is clearly illustrated by Fig. 5. The lower curve is projected to show the approximate percentage reduction and pounds sulphur removed, by 10 lb. of fused soda ash per ton of molten iron with sulphur contents varying from 0.10 to 0.01 per cent. The reduction indicated represents about average expectancy in actual foundry practice, under favorable conditions and with proper handling. (Data from which the chart is plotted were selected from practical operating results, including some tests on electric-furnace iron.)

Correct Handling Especially Important with Low-sulphur Irons.—The gradual loss in "percentage reduction" with lower sulphur irons, as indicated by the chart, is attributable to: increase in the ratio of slag and/or entrained silicates to total sulphur present; relative effect of reactions with the lining and FeSi in reducing the activity of the slag, compared to percentage of sulphur present; and effect of temperature drop upon reactions in relation to percentage of sulphur in the iron.

One purpose of Fig. 5 is to show the relatively greater effect of any free slags or entrained silicates, and/or improper handling upon the results obtained with low vs. higher sulphur irons. To illustrate: assume a condition wherein 10 lb. of reagent would reduce a 0.07 per cent sulphur to 0.042 per cent, that is, 40 per cent reduction instead of 54 per cent as in the chart. Under similar conditions it is figured that an 0.035 per cent sulphur iron would be reduced only about 25 per cent or to 0.026 per cent, as compared to 0.019 per cent in the chart. Thus the necessity for correct handling is evident, especially when treating lower sulphur irons or when attempting maximum desulphurization of higher sulphur metal.

Oxidation of Sodium Sulphide.—Reaction 3 (Na_2S to SO_2) represents any conversion of sulphides in the slag to gaseous sulphur compounds, which escape into the air, and to represent oxidation at the slag surface. The speed of this reaction, as indicated by the amount of sulphur fumes evolved, varies widely with changing conditions.

Observations made in practical open-hearth operating tests, when pouring the desulphurizing slags into the hot furnace along with the molten iron, indicate that most of the sulphur held in the sodium slag is immediately oxidized to SO_2 and passes off in the furnace gases.

Reversion of Sulphur from Slag to Metal.—Reaction 4 (Na_2S to FeS) is taken to represent all manner of reversion of sulphur from the slag back into the metal bath. The speed of this reaction, expressed in terms of its effect upon percentage of sulphur in the metal bath, increases as total acids increase in the slag. Conversely, desulphurizing gradually slows up as the slag is acidified, until finally the effect of reaction FeS to Na_2S would be overbalanced by the reverse reaction "Na_2S to FeS." This results in a net increase in the return of sulphur back from the slag or a rise in sulphur content of the metal. With deep baths such as in

ladle treatment, where the slag-metal-surface area is small in relation to the mass of metal, the reverse reaction is of relatively minor importance in determining the final sulphur. In shallow baths, however, as in air-furnace desulphurizing, where the metal depth varies from 10 in. to zero
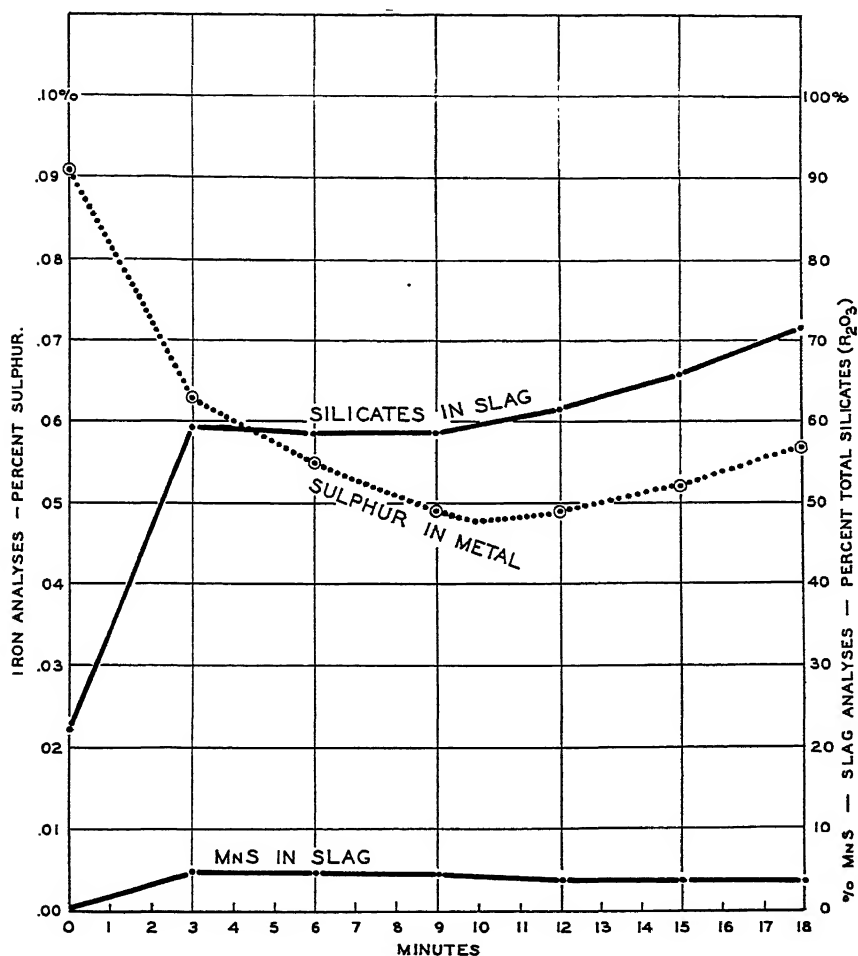
FIG. 6.—PROGRESS OF DESULPHURIZING (AIR-FURNACE PRACTICE).
Action of soda slags in air-furnace malleable practice, 10 lb. fused soda ash per ton. Dotted line indicates rate of sulphur removal to minimum of 0.049 per cent at 10 minutes after treatment, and thereafter, rate of return of sulphur back into metal bath as total silicates, shown by upper black line, increase in slag.
Lower black line represents absorption of manganese sulphide in slag.

and where the slag is acidified by roof drippings and corrosion at the slag line, the end results may be affected in large part by reversion of sulphur from the slag back into the metal bath.

It will be understood that any or all of the reactions go on in the slag and between the slag and metal bath at one and the same time. The

foregoing is intended simply to illustrate the combined effect of all reactions upon the sulphur contents of the metal bath, at various stages during the progress of desulphurization.

Reactions Illustrated by Air-furnace Test.—Something of the speed and order of the combined effects of the various reactions is nicely illustrated by data obtained some years ago in a series of desulphurizing tests carried out in air-furnace practice. In these tests the furnace slag was thoroughly skimmed off and 150 lb. of fused soda ash (10 lb. per ton of metal) was added to the bath. Iron and slag samples were taken at 3-minute intervals over a period of 18 minutes and analyzed. The results are

TABLE 2.—*Progress of Desulphurizing in Air-furnace Tests*

Sulphur	Before Treatment, Per Cent	After Adding 10 Lb. Fused Soda Ash per Ton, Per Cent					
		3 Min.	6 Min.	9 Min.	12 Min.	15 Min.	18 Min.
Sulphur in metal........	0.091	0.063	0.055	0.049	0.049	0.052	0.057
Points removed.........		0.028	0.036	0.042	0.042		
Points returned to metal.						0.003	0.008
Reduction, net per cent.		31	40	46	46	43	37

SLAG ANALYSIS

Composition	Initial Soda Slag						
SiO_2 in slag............	14.03	45.96	45.97	45.26	46.71	50.63	55.76
FeO in slag............	3.68	5.24	5.37	5.89	5.85	6.28	6.61
Al_2O_3 in slag...........	4.37	8.01	7.41	7.37	9.03	9.10	9.33
Silicates..............	22.08	59.21	58.75	58.42	61.57	66.01	71.70
MnS in slag............	0.24[a]	4.78	4.83	4.17	3.77	3.70	3.59

[a] All Mn in the slag reported as MnS.

shown in Table 2 and illustrated by curves in Fig. 6. It is apparent in this test that most of the initial drop in sulphur from 0.091 to 0.063 per cent during the first 3-min. period was due to direct absorption in the soda slag of suspended manganese sulphide. This is indicated by the sudden increase of MnS in the slag from 0.24 to 4.78 per cent within this period. After suspended sulphur compounds were washed out, removal of sulphur was limited to reactions FeS to Na_2S and/or MnS to Na_2S, which continued at a slower and gradually decreasing rate, to a maximum percentage reduction at about 10 min. From this point on there was a gradual return of sulphur from the slag back into the metal bath, Na_2S to FeS, as the percentage of silicates (total acids) increased in the slag.

The reversion of sulphur from the slag back into the metal bath would be accelerated in an air furnace; first, by the continued boiling action

caused by the flame and, second, by the relatively large metal-slag surface area in relation to the total mass of metal. However, with practical desulphurizing operations in a 30-ton ladle, where the slag gradually quiets down as the reactions proceed and where the ratio of slag-metal surface to the total mass of metal is limited, this reaction (Na_2S to FeS) would actually play a very small part in determining the final sulphur contents.

Affinity of Soda Slags for Silicates.—The sudden increase of silicates (SiO_2, FeO, Al_2O_3) in the slag—from 22 to 59 per cent—and the increase in MnS from 0.24 to 4.78 per cent during the first 3-min. period of the test clearly illustrate the pronounced affinity of soda slags for silicates and the very rapid rate at which entrained compounds are washed out of the metal bath by the alkali slags.

The rapidity of the reactions with silicates, compared to the slower reactions with FeS, explains how the presence of free slag and entrained silicates always decreases the percentage of sulphur reduction. As Fig. 5 shows, this effect is more pronounced with lower-sulphur irons. With excess silicates, sufficient to more than acidify the slag, reductions in sulphur will be limited mostly to that removed by absorption of MnS in the slag bath. Even small amounts of silicates tend to "kill" the slag, thereby retarding the reactions.

Effect of Carbon, Silicon, Phosphorus, Etc. upon Reactions.—Authoritative data on the effect of the normal elements occurring in cast iron upon the reactions of soda slags is limited. It may be assumed, however, that all elements, to the extent that they may add needed fluidity, act to promote the reactions. Manganese promotes desulphurization (Table 2). Its effect is pronounced, at least to the extent that it exists as insoluble MnS or reacts to form it. Though an aid within certain limits, high manganese is not essential to successful desulphurization.

Carbon when present in the amounts occurring in ordinary cupola metal (3.25 to 3.50 per cent) serves to promote the reactions. Low-carbon cupola metal is more difficult to desulphurize, and no desulphurization of steel will generally result with ladle treatments. However, the alkalies accelerate the desulphurizing reactions of basic open-hearth slags. Excess carbon in molten pig iron that would be thrown out as kish has a retarding effect, as previously explained.

It is believed that the action of carbon in promoting desulphurization (with alkali slags) is due primarily to its effect in controlling fluidity rather than to any part in the chemical reactions. No determinable loss of carbon occurs with desulphurization. If any, it is so small that it will not generally show in commercial laboratory check determinations of samples before and after treatment.

The percentage of combined carbon in ordinary cupola cast iron (1¼-in. test bar) will be gradually lowered with desulphurizing to the

extent of 25 to upwards of 60 per cent of the sulphur present, but will be increased with further desulphurization. This is due no doubt to the predominance of oxidizing reactions occurring with the excess of free alkali required for maximum desulphurization.

The alkalies react with silicon (FeSi) held in cast iron to form silicates. To that extent, silicon consumes reagent, and more, tends to kill the soda slag. Thus any excess silicon over that serving to increase fluidity and promote contact between metal and slag may act to retard desulphurization.

Effect of Smelting Practice.—It has been observed in practical operations that irons melted or made with high-lime (basic) slags are more difficult to desulphurize than irons of similar composition made with more acid slags. Several theories have been suggested as explaining these phenomena—to what extent it exists and why are not known. However, desulphurizing would appear to be more efficient or less costly when applied to blast-furnace metal made with lean slags.

Time Required for Reactions.—Time required for completion of the reactions will vary widely. It may range from a minimum of 4 min. upward, depending upon the extent of desulphurizing required, the manner of carrying out the process and the activity of the reagent. From the explanations of the reactions it is seen, however, that the operations should always be carried out as quickly as possible.

Promoting Contact between Slag and Metal.—The most important factor in efficient desulphurizing, aside from temperature and the reagent itself, is rapid and intimate contact between slag and metal bath. In the absence of heat over the slag bath, boiling or stirring action can be effected in large-scale operations only in one or two ways; by the composition and/or form of the reagent; by the stream of iron flowing into the bath.

As previously mentioned, the stream of iron flowing into the desulphurizing ladle promotes slag-metal contact. This results both from the physical effect of the stream in stirring the metal and from its action in whipping portions of the refining slag down into the metal bath. This not only increases the amount of surface contact between metal and slag but also makes for more effective contact because of the pressure of the overlying metal. Moreover, decomposition of the reagent under the metal surface, with the consequent evolution of gases, acts to further increase surface contact.

Caustic soda, because of its lower melting point and greater activity as compared to soda ash, makes for more violent boiling action or more rapid contact between metal and slag. Boiling may be prolonged in some cases by additions of soda ash and other carbonates to the caustic (Sulfex). With fused soda ash (Purite), boiling action is prolonged by gradual melting of the 2-lb. briquets.

Purpose of This Discussion

It is hoped that this outline of the reactions applying in desulphurizing molten iron with the alkalies has served to illustrate: (1) the importance of selecting the reagent in relation to the character of the metal to be treated, and the extent of desulphurizing required; (2) the necessity of correct equipment design and layout for carrying out the process in an efficient manner; (3) the importance of carrying out the operations strictly in accordance with a fixed schedule. found by experience to produce efficient and consistent results.

DISCUSSION

(R. A. Lindgren presiding)

R. A. LINDGREN,* South Chicago, Ill.—It is rather difficult, I suppose, to get any blast-furnace operator to admit that he has any problems in regard to desulphurizing pig iron. None of us will admit that we ever make any high-sulphur iron. We have played around with the idea of desulphurizing iron, along the line of helping out the open-hearth man when he has to make some heats that call for especially low sulphur, and we have had this question asked us by the open hearth man: Suppose a ladle or two of desulphurized iron is put into the open-hearth furnace; what effect will the slag have on the open-hearth bath?

G. S. EVANS.—Some operators regularly use fused soda ash in the open hearth at the rate of 200 to 300 lb. per charge in 100-ton furnaces. The object of this particular application is to reduce foaming. On certain types of foamy slags, the effect is rather pronounced and is permanent, while on other types of slags foaming may be arrested for only a short period. On the whole, this application is proving profitable at plants with certain fuels with which foaming is more apt to occur. I think it would require an open-hearth man to explain this effect upon the slag.

As explained in the earlier part of my paper, the recommended practice for desulphurizing would include skimming off the alkali slag before pouring the metal into the open hearth. This is the practice now followed at plants where it is the regular practice to desulphurize off sulphur heats. Some experiments have been conducted wherein the desulphurizing slag is poured into the blast furnace along with the metal. However, I do not know of any authentic records comparing analyses of the two methods of applying soda-ash desulphurizing.

It is known that sodium sulphide is rapidly oxidized to sulphur dioxide under certain conditions, passing off as a gas. This reaction is fairly rapid under highly oxidizing conditions and it is my opinion that there would be comparatively small reversion of sulphur into the metal bath in adding the soda slag containing sulphur in this form to the highly oxidized slag bath existing in the open hearth at the time liquid metal is usually added. I have seen records of several heats where this method of treatment was followed on high-sulphur casts wherein the initial sulphur tests from the open-hearth bath compared favorably with regular tests with molten pig iron of normal sulphur contents. On the other hand, I hardly think that anyone is prepared to answer the question on the basis of data available at this time.

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* Superintendent, Blast Furnace Dept., Wisconsin Steel Works, International Harvester Co.

R. L. COLLIER,* Barberton, Ohio.—May I add a comment in regard to that?   The moment your alkaline slag goes into the open-hearth furnace it comes in contact with your flame, and your Na₂S will be oxidized, passed out over your ports.

R. H. SWEETSER,† New York, N. Y.—What effect does the alkaline slag have upon the brick lining—the lining of the ladle or the lining of the mixer?

G. S. EVANS.—As explained in the paper, maintenance of ladle lining constitutes a considerable part of the total cost of desulphurizing, sometimes running upward of 15¢ per ton of metal treated with the use of caustic soda for maximum desulphurizing. It is impractical to attempt desulphurization in the mixer, as the cost of maintenance would be prohibitive.   On the other hand, it is the practice at some plants to add small quantities of fused ash in the mixer for breaking up islands or liquefying heavy slags.

In acid open-hearth practice even small additions, 3 to 4 lb. per ton of metal charge, would exert a noticeable cutting action at the slag lining.   This is due more to the action of soda ash in increasing the activity of the whole slag than to any direct reactions between the alkali present and the lining.   In basic open-hearth practice, I think it can be said that there would also be somewhat increased tendency to react with the lining at the slag line.   However, present users report that this is negligible from the standpoint of final cost.   It is generally found that the length of heats will be slightly shorter with the use of soda ash, and this saving in furnace time is thought to effect some saving in over-all costs of furnace lining.

R. H. SWEETSER.—Would it be possible to make a brick that would better withstand erosion?

G. S. EVANS.—Strange as it may seem, high-silica, low-alumina bricks withstand soda slags better than bricks of more basic character.   Magnesite will not withstand the slag in combination with iron or copper oxides.   Sillimanite brick has been found to withstand desulphurizing slags.   However, the increased life of ladle lining will not ordinarily justify the added cost of this type of refractory except in special equipment where the cost of laying up the lining may be particularly high.   The ordinary steel-ladle brick, such as Dando, which usually are made very dense and hard burned so that they tend to expand, sealing the joints as they heat up, have generally proved more economical in practical operations.

R. L. BOWRON,‡ Birmingham, Ala.—Results obtained in our duplex method by the use of iron that had been desulphurized by the use of soda ash may be of interest.   In a number of casts used, it was indicated that the slag on the metal after being blown was more liquid and beyond the point of being controlled.   Owing to the liquid condition, the slag followed the metal into the furnace and poisoned the slag to such an extent that it gave us more trouble in eliminating the phosphorus than the small benefit derived from the reduction of the sulphur.

G. S. EVANS.—I think that the difficulties described by Mr. Bowron can be attributed to the failure to thoroughly skim off the desulphurizing slag before adding the metal to the converter for blowing.   It is known that even small quantities of soda slags will result in excessive oxidation of the metal in acid converter practice and this no doubt produced a larger volume of siliceous slag, which may explain the bad affect of the slag in the open hearth.

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* Columbia Alkali Co.
† Consulting Engineer.
‡ Tennessee Coal and Iron Co.

R. A. LINDGREN.—It seems to me that the paper does not sufficiently stress the matter of the influence the temperature of the metal has on desulphurization. From our experience I would say that the matter of temperature is of prime importance and the efficiency of the desulphurizing agent is entirely dependent on the temperature of the metal at the time of treatment. It does not clearly bring out the fact that if the metal is held too long after being treated there is a definite trend toward a reversal of the desulphurizing reaction. From an operating standpoint, I feel that this is of prime importance in the application of the process.

G. S. EVANS.—The reactions are more active at higher temperatures. I mention the importance of selecting the reagents with reference to metal temperature and the extent of desulphurizing required. At temperatures of 2500° and over, soda ash is generally preferable for desulphurizing up to 60 per cent of the sulphur present. On lower-temperature irons caustic soda or mixtures of caustic soda and soda ash will prove generally more economical.

As explained in the discussion of the reactions, there is a rather pronounced reversal of sulphur from the slag back into the metal when the slag is acidified, as in air-furnace malleable practice with a bath depth ranging from 0 to 10 in. In large ladles, however, it has been found that this reversal reaction is secondary as compared to the importance of first skimming the metal of slag and siliceous inclusions. It has been found in practical checks that where desulphurizing failed the failure was due not so much to reversal as to excess slag inclusions.

R. L. COLLIER.—There is a happy medium in regard to temperature as far as percentage of sulphur reduction is concerned. We find that at very low temperatures our reductions are slight, probably because of less contact between the material and the soda ash used; with high temperatures the reactions are too fast; so that in between occurs the best percentage of results.

Combined Carbon—A Controlling Factor in Quality of Basic Pig Iron

By Ralph H. Sweetser,* Member A.I.M.E.

At the joint session of Blast Furnace and Open Hearth Committees, April 7, 1937, at Birmingham, the subject of the quality of basic open-hearth pig iron was so well presented and discussed from so many different viewpoints that it was the general opinion that progress had been made and that such meetings were conducive to the advancement of the art of making pig iron of the right quality for the open-hearth man to produce the most satisfactory quality of steel.

It was agreed that there is a decided differentiation between the chemical analysis of pig iron and the "quality" of pig iron. Paul J. McKim said that open-hearth furnace operators frequently make reference to certain types of iron as "bad iron," "dirty iron," "cold metal," etc., claiming that when using these irons, although they are within specified chemical analysis, it is impossible to produce quality steel. Mr. McKim gave a list of the suggested causes of those "certain types" of bad irons that have a thoroughly respectable analysis but a thoroughly disreputable character. Another open-hearth man, P. A. MacIsaac, of Nova Scotia, said that:

The effects of iron that is below standard in analysis or in that mysterious property called quality, are well known to all open-hearth operators. It has been shown that iron of this type results in the production of steels on which the rejections of finished product run high. What is to be done about it? I would say that the burden of producing high-quality iron should be placed squarely on the shoulders of the blast-furnace man, even as that of making good steel is shouldered by the open-hearth man.

It is the purpose of this paper to bring out into the open this "mysterious property called quality"; that is, in those "certain types" of basic pig iron that make it impossible to produce quality steels; and at the same time to point the way for the blast-furnace man to be able to shoulder the burden that Mr. MacIsaac and all other open-hearth men and foundrymen have placed upon him.

Silicon, sulphur, phosphorus and manganese are not the guilty elements because these are known, specified and usually kept within the

limits of desired analysis. It cannot be any particular combination of these metalloids, because open-hearth men have found that within certain limits of each of these elements they can get best results for quality steel; and the blast-furnace men have produced basic pig iron within these specified limits. The troubles for open-hearth men have sometimes come, without warning, when the pig iron was well within the limits set for all four of these metalloids; the troublemaker was some other element.

For a long time I had suspected that the unknown element was carbon in one of its numerous forms, a plausible theory because carbon is the most abundant metalloid in pig iron, but for some reasons it has been kept out of specifications. Sometimes it takes a long time to gain attention for a new idea, and still longer to have it generally accepted. For 10 years I waged my "clean coal" campaign before it was accepted by the coke-oven and blast-furnace men and the A.I.M.E. A much longer time than that was required to obtain recognition of the fact that carbon is an all-important factor in the quality of pig iron. At a meeting in Atlantic City 23 years ago the specifications for merchant pig iron were discussed by a committee of the American Society for Testing Materials and the pig-iron producers. When I mentioned graphitic carbon and combined carbon I was so quickly and forcefully squelched that it was a long time before I mentioned the subject again in public. The TRANSACTIONS of the A.I.M.E. for the past several years record the fact that I have persistently asked the open-hearth men how much carbon they want in basic pig iron, and why they want it. The answer has been: "If we specify carbons can the blast-furnace men give us what we ask for?" And there the matter has rested until the blast-furnace men have been asked, "What is to be done about it?"

I now believe something can be done. Total carbon is the most abundant metalloid in basic pig iron, but we have not paid much attention to it, perhaps because within the specified limits for silicon, sulphur, phosphorus and manganese in making standard basic pig iron at a furnace using the same fuel regularly there is not much variation in the percentage of total carbon from cast to cast and from day to day, as shown in Fig. 2. At the same furnace there is no appreciable difference in the amount of total carbon in the good iron and the admittedly bad iron; this was brought out in a graph that I showed at Birmingham, which is herewith reproduced as Fig. 1. The last 15 casts show an average of 4.33 per cent total carbon (max. = 4.45, min. = 4.23). As far as we know now, the total carbon in basic pig iron cannot be varied at will in the blast furnace, but plans are afoot for doing so.

COMBINED CARBON DEFINITE INDICATOR

Combined carbon, on the other hand, can be controlled in basic pig iron just as much as the sulphur is controlled, and it would seem as though

these two metalloids can both be handled in the same way: as a rule, low combined carbon and low sulphur go together. After participating in several research projects similar to those reported by Brewster[1] and Joseph,[2] and many years of making basic iron for some high-quality open-hearth steel men, and after a recent review of the records, I am brought to the conclusion that the percentage of combined carbon in the pig iron is the one definite indicator of the true character, that "mysterious property called quality," of basic pig iron. Whether or not the percentage of combined carbon *per se* is the controlling factor I do not know, but I do know that when the amount of combined carbon goes above a certain per cent the quality of the steel sheets goes down below the standard; and I do know that the percentage of *combined* carbon in the pig iron, *not* the total carbon, is the one chemical analysis that can be safely used as an indicator of its present quality, of the past conditions surrounding its production inside the blast furnace, and of its future behavior inside the open-hearth furnace and the rolling mill.

The term "pig iron" in this paper refers only to hot metal, or "direct metal," going from the blast furnace to the open-hearth furnaces.

This controlling influence of the combined carbon was first demonstrated at the Ashland (Ky.) Division of The American Rolling Mill Co. during the summer of 1924, when it was my good fortune to participate in research work that involved the whole steel plant, including a blast furnace that was to be blown out within two weeks and with which we were allowed "to do anything we pleased." The aim of the test, as stated on the order sheets, was "to investigate the influence of varying amounts of graphitic carbon in the pig iron on the surface of Armco ingot iron and steel sheets as rolled in the mill, especially in connection with surface defects on steel sheets." A similar test had been conducted at the Columbus furnaces of the same company the previous year, but there the iron was all "good iron" shipped as cold pig iron (machine cast), and only total carbons and temperatures were studied. A partial report of this test was presented in my paper at the Round Table on Carbon in Pig Iron at the annual meeting in New York, February 1927.[3]

As in many other research problems, we found something different from our announced aim. At Columbus we sought hearth temperatures and total carbons; at Ashland we sought the influence of hearth temperatures on graphitic carbon; but, the surface of the finished sheets showed us that it was *combined carbon* that we should look for.

TESTS

Temperatures.—Temperatures of the molten iron were taken between the skimmer and the dam as the iron flowed from the iron notch at cast;

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[1] References are at the end of the paper.
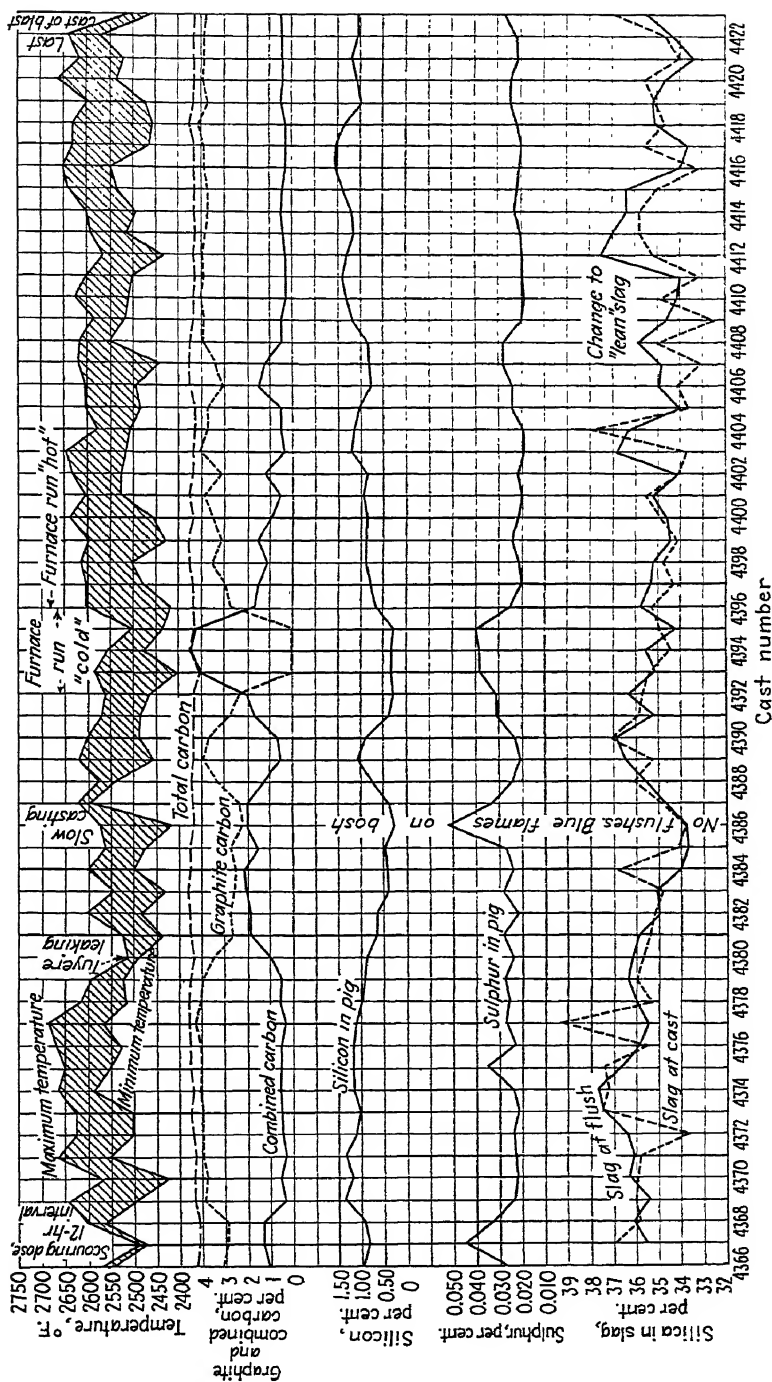
Fig. 1.—Temperature variation in the cast.
Reprinted from Open Hearth Proceedings, 1937, A.I.M.E.

both optical and thermocouple pyrometers were used, and where the surface of the molten iron was clear, the readings checked closely. The platinum-rhodium thermocouple used was similar to that described by Joseph[2] but we used a fused quartz instead of a porcelain protecting tube. Observations were taken and recorded every 60 sec. throughout the cast.
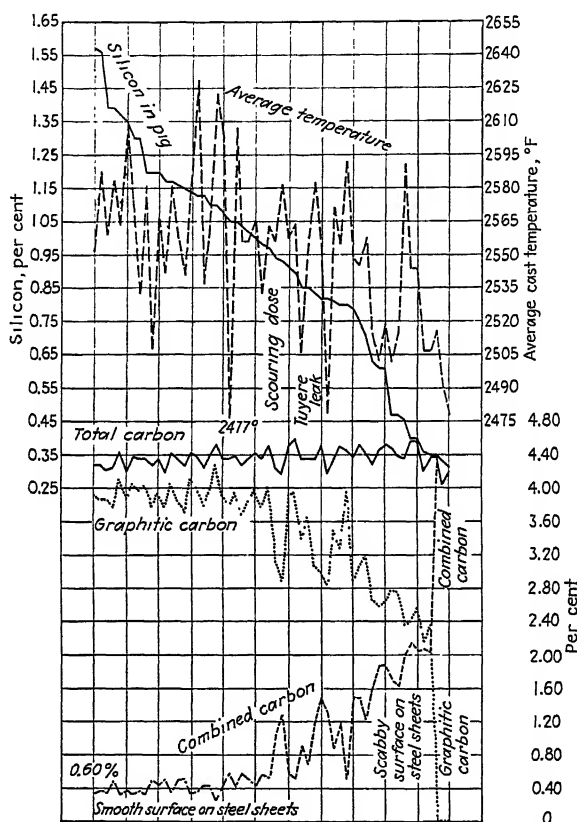
FIG. 2.—RELATION BETWEEN SILICON TEMPERATURE AND COMBINED CARBON IN PIG IRON.
Reprinted from Open Hearth Proceedings, 1937, A.I.M.E.

Sampling the Iron.—Samples of pig iron were dipped from the runner with a regular sampling ladle and poured into a warm cast-iron mold, as is usual practice. We had found that total carbons, graphitic carbons and combined carbons agreed fairly well whether the sample was taken at the runner, at the hot-metal ladle, or, for machine-cast pig iron, in the cold pig. A set of samples poured into sand molds was also taken for the determination of tensile strength, but as far as I know these results were not tabulated. Some samples were analyzed for oxygen, but it was soon decided that the oxygen content did not appear to be a controlling factor, and this analysis was discontinued.

Charting the Results.—In Fig. 1 the temperatures of each cast and the analyses of iron and slag are charted in consecutive order, beginning with the 8 a.m. cast, Aug. 6, 1924, and ending with the 8 p.m. cast Aug. 15, 1924, when the furnace was blown out. The bad effects of a "scouring dose," of a leaking tuyere, of a too limy furnace, of an overburdened and "cold bottom" furnace, are clearly shown in Fig. 1.

The results were then arranged in the descending order of the silicon content, showing the *average* temperature of each cast and the percentages of total carbon, graphite carbon and combined carbon as in Fig. 2. This seemed to indicate that the combined carbon was a controlling factor in the production of smooth-surface sheets.
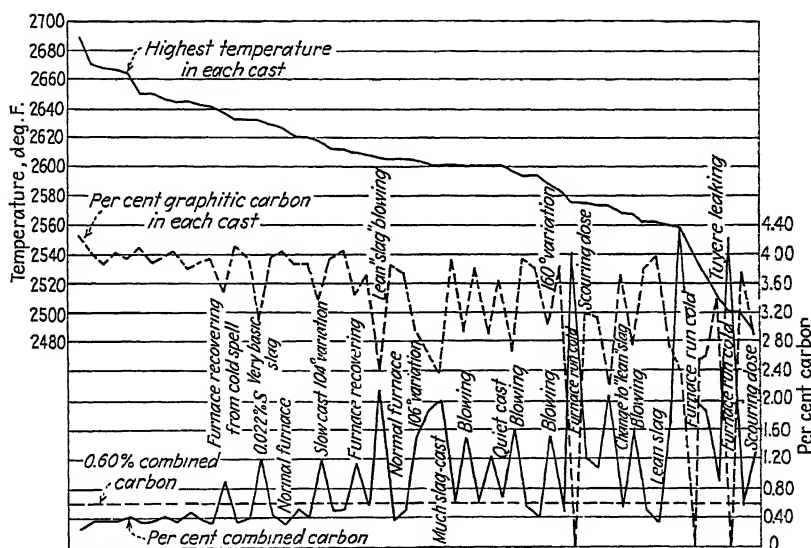
FIG. 3.—SHOWING THAT TEMPERATURE ALONE DOES NOT CONTROL.

In Fig. 3 the carbons were plotted against the highest temperature in each cast, and it appears that temperatures alone do not control the quality of the sheet steel; and Fig. 4 shows that the highest temperature does not always give the lowest sulphur, or the highest total carbon.

In plotting the percentage of combined carbon against the highest temperature in the cast as in Fig. 5, there seems to be a connection between the highest temperature of a cast and the amount of combined carbon in that cast; the average temperature throughout a cast does not appear to control the percentage of combined carbon as much as does the *highest* temperature. Evidently, there are certain changes in running the furnace that may affect the average and maximum temperatures of a cast but not necessarily affect the combined carbon beyond the permissible limit.

It would be interesting to know what effect the half-hour checking of the red-ore furnaces of the Birmingham district has on hearth temperatures and percentages of combined carbon.

Total carbon	4.57%	4.48%	4.49% 4.47% 4.46%		4.50%
Silicon	0.70	0.70	0.63 0.70 0.74		0.75
Sulphur	0.036	0.031	0.039 0.038 0.029		0.049
Temperature	2518°	2526°	2538° 2541° 2543°		2569°
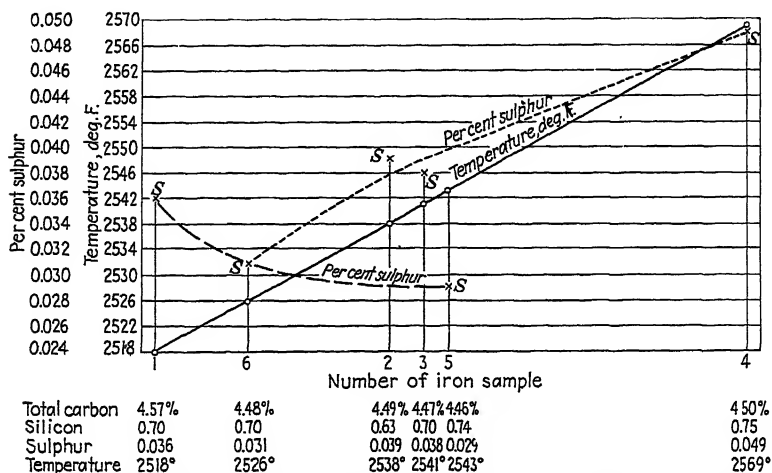
Fig. 4.—Showing that highest temperature does not always give the lowest sulphur or the highest total carbon.

At Ashland when the percentage of combined carbon, for any cause whatsoever, went above 0.60 per cent in the hot metal (made from Lake Superior ores) that went to the open hearth, there would be scabs on the
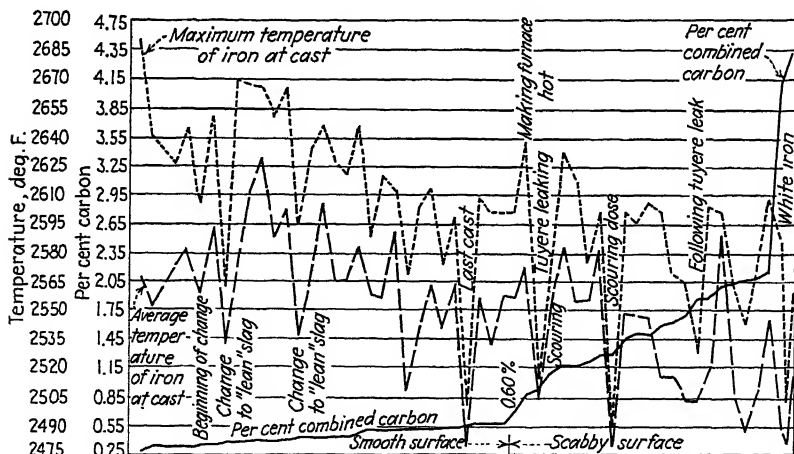
Fig. 5.—Combined carbon vs. maximum temperature.

sheets made from that steel. In the test described above it was easy to trace the steel all the way through the mill. Other districts may have a different maximum limit for combined carbon in "good" basic iron. Possibly hot metal from eastern magnetites, or from Southern ores, may

TABLE 1.—*Analyses*

CASTS ARRANGED ACCORDING TO HIGHEST TEMPERATURE

Cast No.	Highest Temperature, Deg. F.	Composition, Per Cent					Remarks
		Si	S	Total Carbon	Combined Carbon	Graphitic Carbon	
4377	2689	1.10	0.024	4.53	0.28	4.27	Highest in test (total C, 2689°; optical, 2685°) O₂, 0.044 per cent
4376	2670	1.17	0.023	4.42	0.37	4.05	
4371	2667	1.35	0.023	4.28	0.38	3.90	
4374	2666	1.13	0.024	4.39	0.38	4.01	Highest average temperature, 2628°.
4420	2664	1.08	0.025	4.36	0.42	3.94	Much kish in air when poured open hearth.
4375	2651	1.14	0.035	4.45	0.36	4.09	
4416	2651	1.56	0.021	4.26	0.38	3.88	
4422	2646	1.05	0.022	4.39	0.43	3.96	Blowing at cast.
4403	2645	1.20	0.019	4.36	0.33	4.03	Blowing second highest tensile strength
4415	2645	1.39	0.022	4.28	0.49	3.79	
4369	2643	1.38	0.023	4.30	0.40	3.90	
4417	2641	1.57	0.020	4.26	0.33	3.93	
4400	2637	0.81	0.022	4.38	0.89	3.49	O₂, 0.032 per cent; CO, 0.012 per cent.
4418	2633	1.37	0.022	4.45	0.33	4.12	Long slow cast.
4372	2632	1.10	0.024	4.39	0.43	3.96	O, 0.043 per cent; CO, 0.010 per cent.
4402	2632	0.84	0.022	4.36	1.20	3.10	Blowing.
4373	2628	1.00	0.022	4.42	0.44	3.98	O₂, 0.061 per cent; CO, 0.0.008 per cent.
4410	2626	1.30	0.019	4.39	0.33	4.06	First part of cast the hottest.
4389	2620	1.02	0.021	4.36	0.51	3.85	Temperature rose 165° in 6 min. O₂, 0.051 per cent.
4421	2620	1.20	0.022	4.36	0.45	3.91	Blowing.
4407	2618	0.80	0.028	4.50	1.20	3.30	Slow tap.
4408	2613	0.80	0.028	4.47	0.51	3.96	O₂, 0.044 per cent; CO, 0.012 per cent.
4378	2613	0.97	0.026	4.54	0.53	4.01	Furnace same all night. Much kish.
4398	2610	0.84	0.022	4.45	1.00	3.45	
4405	2608	1.04	0.024	4.28	0.57	3.71	O₂, 0.036 per cent; CO, 0.008 per cent.
4384	2607	0.40	0.024	4.57	2.15	2.42	Much slag and "surging" at cast. O₂, 0.022 per cent.
4411	2606	1.39	0.020	4.23	0.36	3.87	Highest tensile strength.
4414	2606	1.17	0.023	4.28	0.52	3.76	
4406	2605	0.75	0.024	4.53	1.50	3.03	
4382	2603	0.61	0.022	4.54	1.88	2.66	O₂, 0.061 per cent; CO, 0.014 per cent.
4387	2601	0.46	0.033	4.36	2.00	2.36	Much cinder soon after iron came.
4401	2601	0.91	0.020	4.51	0.59	3.92	
4397	2601	0.79	0.020	4.39	1.46	2.93	Blowing.
4419	2601	0.99	0.025	4.36	0.57	3.79	
4368	2601	0.93	0.032	4.18	1.28	2.90	Blowing. "Black scum."
4390	2601	0.85	0.023	4.36	0.69	3.67	"Nice quiet cast."
4396	2601	0.63	0.025	4.28	1.60	2.68	Blowing.
4379	2598	0.90	0.028	4.58	0.54	3.94	Middle of cast the hottest.
4413	2595	1.13	0.021	4.25	0.43	3.82	"Blowing bad."
4399	2595	0.82	0.024	4.53	1.50	3.03	First part of cast the hottest.
4409	2588	1.16	0.020	4.36	0.51	3.85	
4393	2585	0.33	0.038	4.03	4.03	0.00	Minimum temperature—2407°. Lowest total C.
4388	2576	0.71	0.024	4.42	1.22	3.20	O₂, 0.048 per cent; CO, 0.016 per cent.
4366	2576	0.94	0.027	4.24	1.10	3.14	Scouring dose. Dirty flushes.
4386	2575	0.36	0.052	4.26	2.08	2.18	Part of cast at only 2414° F.
4404	2575	1.15	0.019	4.26	0.54	3.72	Quite even temperature.
4391	2570	0.47	0.031	4.39	1.63	2.76	
4370	2569	1.20	0.022	4.29	0.52	3.77	O₂, 0.054 per cent; CO, 0.011 per cent.
4412	2563	1.30	0.020	4.36	0.37	3.99	
4385	2563	0.47	0.027	4.49	1.70	2.79	Slow tap. Hearth getting cold. O₂, 0.031 per cent.
4392	2562	0.35	0.031	4.39	2.01	2.38	Part of cast 2427° (total C) 2421° Op.
4394	2559	0.35	0.038	4.40	4.40	0.00	
4383	2543	0.40	0.028	4.61	2.05	2.56	Highest total carbon; much slag.
4381	2528	0.61	0.028	4.46	1.86	2.60	Cast following leaking tuyere.
4380	2514	0.85	0.024	4.36	0.93	3.43	Tuyere leaking.
4395	2502	0.32	0.040	4.22	4.22	0.00	
4423	2501	1.05	0.027	4.36	0.57	3.79	
4367	2489	0.82	0.045	4.16	1.30	2.86	Scouring dose; 12 hr. apart.

have a different maximum of combined carbon beyond which the iron would be "bad" for making steel.

Judging from my experience with the grading of merchant pig iron before the introduction of pig machines, I believe that a study of the effects of combined carbon in other steelmaking irons and in foundry irons is justified.

Low Sulphur

At the Birmingham meeting it was stated that the open-hearth men wanted less than 0.020 per cent sulphur in basic pig iron, and the question was asked what this would mean to the blast-furnace men.

In the light of what has been shown about the influence of the combined carbon, I doubt very much whether such low sulphur is really what is needed. The analyses in Table 1 show that many casts with low combined carbon had sulphurs between 0.020 and 0.025 per cent, but one cast (No. 4384) had 0.024 per cent sulphur, but also had 2.42 per cent combined carbon. Any open-hearth man that gets 0.025 per cent sulphurs ought to be contented. It is for the open-hearth men to show that the steel plant will save money if the sulphur in the pig iron sent to the open-hearth furnaces has less than $7\frac{1}{6}$ oz. of sulphur in a ton of pig iron, instead of 9 oz. This request should be further investigated.

Uneven Operation in Test

In looking at the charts of this test, open-hearth men might think— and some probably say—that it was very irregular blast-furnace practice. It was—with the exception of the leaking tuyere, the practice was purposely made irregular, so that the effects of "off" iron might be traced. Seldom, if ever, is a blast furnace deliberately made to produce "off iron," but that is exactly what took place when we made the temperature tests at No. 1 Ashland furnace of The American Rolling Mill Co. in 1924. At the Columbus furnaces the previous year, continuous observations were made for a week, but the furnaces were working too smoothly for any study of "off" iron. Fig. 1 shows what happens when a blast furnace is run as cold as any of us dared to run it. The furnace made iron with silicon as low as 0.32 per cent without forcing the sulphur above 0.040 per cent. All the carbon was combined carbon and of course the iron was all white. This was done by running the furnace with a "cold bottom," simply by a heavy burden and a limy slag.

Acknowledgments

research men who participated in these most interesting investigations; at Columbus the list would include men from the U. S. Bureau of Mines and from the staff at Ohio State University. Only by such widespread cooperation can the subtle influences of carbon in pig iron be discovered.

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DISCUSSION

(R. K. Clifford presiding)

T. S. WASHBURN,* Indiana Harbor, Ind. (written discussion).—Mr. Sweetser is to be congratulated on the unusually complete data covering the composition and temperature of iron produced under abnormal blast-furnace operating conditions. The characteristics of iron from a sequence of casts that vary throughout the range of basic pig-iron composition are of considerable interest to both blast-furnace and open-hearth men, and the data submitted in this paper demonstrate clearly the relationship between the temperature, analysis, and structure of basic iron.

In Fig. 2 the author has shown graphically the casts plotted in order of decreasing silicon content. This graph demonstrates the general relationship between the silicon and the temperature of the iron, and shows the normal relation of decreasing silicon content with decreasing temperature. The total carbon, and the combined carbon with the reciprocal value for the graphitic carbon, have also been plotted on this graph, and the curves for these variables demonstrate that there is no change in the total carbon content but that the percentage of combined carbon increases with decreasing silicon content of the iron. This relation between the silicon and the combined carbon in iron is of course well known, as one of the principal factors governing the distribution of carbon between the two forms is the silicon content of the iron. In interpreting his results, however, the author has apparently considered the ratio of combined to graphitic carbon as an independent variable, instead of as a dependent variable governed by the silicon in the iron, and has attributed results obtained from iron used in the open hearth to the percentage of combined carbon rather than to the silicon content. The effect of variations in the silicon content and the temperature of the iron on open-hearth practice are well recognized and it does not seem justifiable to attribute to a dependent variable such as combined carbon effects that might be more readily explained by silicon and temperature. It is also difficult to see how the form in which the carbon is present in solid iron should have any effect on the performance of liquid iron as charged into the open-hearth furnace.

In Figs. 3 and 5 reference is made to "scabby surface" sheets rolled from steel produced from the casts plotted on the right-hand side of the graphs, which are high in combined carbon and low in silicon content and temperature. It is difficult to interpret these results from the standpoint of steelworks practice, as the term "scabby surface" is usually applied to a defect caused by abnormal conditions when the steel is poured into the ingot molds, and has no direct relation to the melting practice. It is probable, however, that the steel made from these casts was of unsatisfactory quality, as physically cold iron and low-silicon iron often cause a heat to melt too low in carbon,

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* Metallurgist, Inland Steel Co.

and the low silicon content of the iron would also cause the open-hearth slag to be too basic and highly oxidizing. Heats produced under these conditions are often of inferior quality, and sheets rolled from steel of this type may be subject to the defect termed "blisters."

The author has attempted to prove by the data submitted in this paper that combined carbon is a variable heretofore unrecognized in the iron, and that it has an important effect on the manner in which the iron functions in the open hearth. As noted above, this conclusion does not appear justified, as the variation of the silicon and the temperature of the casts is sufficient to explain any of the results obtained from the steel made from these casts.

It is generally recognized by open-hearth operators that the most important variables in iron quality are the temperature and the composition. Iron with a uniformly high temperature when delivered to the open hearth gives the most satisfactory melting results. If the composition of the iron is uniformly maintained within the desired limits for silicon, sulphur, phosphorus and manganese, the proper slag and bath conditions, in so far as they are effected by the iron, will be obtained. It is possible that other factors in iron quality, such as components not currently being analyzed, may prove significant. However, most of the problems in open-hearth operation associated with iron quality can be explained by variations in the known factors governing iron quality.

R. H. Sweetser (written discussion).—The comments and congratulations of Mr. Washburn are much appreciated, but it is evident that in spite of the "unusually complete data covering the composition and temperature of iron under abnormal blast furnace operating conditions," there were not enough results shown in the figures and table to convince him that the author was justified in concluding that "the percentage of combined carbon in the pig iron is the one definite indicator of the true character . . . of basic pig iron."

It is to be regretted that space forbids the publication of more of the thousands of observations of temperatures and analyses made in the test described, but in substantiation of the conclusions reached in the quest for the cause for the troublemaker when all four of the usual metalloids are within the specified limits, the following figures are submitted. There were 14 casts out of the 58 recorded that were wholly within the limits of 0.90 to 1.10 per cent silicon and under 0.040 per cent sulphur; of these, two casts, No. 4366 and No. 4368, gave poor results on the surface of the sheets (see Table 1 for analyses).

Average Analysis of 14 Casts within Limits

Silicon, Per Cent	Sulphur, Per Cent	Combined Carbon, Per Cent	Highest Temperature	Average Temperature
1.00	0.025	0.45	2613° F.	2564° F.

At Least Six Casts with Higher Silicon and Lower Temperature; All "Good"

1.16	0.021	0.49	2565° F.	2525° F.

At Least Six Casts with Lower Silicon and Higher Temperature; All "Bad" Iron

0.84	0.025	1.08	2602° F.	2563° F.

The reasons for the six "bad" casts were as follows: one cast, No. 4368, was after a "scouring dose"; No. 4380, tuyere leaking; No. 4398, No. 4400, No. 4402, No. 4407, running furnace hot after the deliberate bad "chill"; all as shown in Fig. 1.

Neither silicon nor temperature will always control the percentage of combined carbon and the ratio of graphitic carbon to combined carbon (see what a very siliceous slag at cast did to cast No. 4377 (Fig. 1 and Table 1).

It is not "the normal relationship of decreasing silicon content with decreasing temperature," as mentioned by Mr. Washburn, that concerns us in this search for that "mysterious property" mentioned by Mr. MacIsaac (see page 162) that causes rejections in the sheet mill, but it is the *abnormal conditions* within the hearth of the blast furnace that produce deceitful pig iron. I contend that the true indicator of this deceitfulness is the percentage of combined carbon, which the chemist finds in the samples of the pig iron taken in the regular way as the iron flows over the dam at cast.

Mr. Washburn says, "it is difficult to see how the form in which carbon is present in solid iron should have any effect on the performance of liquid iron as charged into the open-hearth furnace." The author cannot see it, either, but has found that the percentage of combined carbon in the solid sample is an *indicator* of the performance of the liquid iron when made into steel sheets.

Composition and Microstructure of Ancient Iron Castings

By Maurice L. Pinel,* Junior Member, Thomas T. Read† and Thomas A. Wright,‡ Members A.I.M.E.

The erroneous, but until recently widely prevalent, belief that iron castings were first made in Europe in the fourteenth century has been adequately refuted in a number of earlier papers;[1,11,12] but except for an unpublished metallographic study by the late William Campbell, and a phosphorus analysis by T. A. Wright of the metal of the Han dynasty cast-iron stove described by Laufer,[2] nothing was known of either the chemical composition or the metallographic structure of the metal of any ancient iron casting, although data on castings of recent manufacture are abundantly available. The metal of the stove, which had been buried in a grave for at least 15 centuries, was so corroded that it seemed inadvisable to publish the results on it until more and better specimens from other ancient castings could be obtained.

During a journey through China, extending from Peking in the north to Canton in the south and Cheng-tu, Ssu-chuan, in the west, in the late summer and autumn of 1936, one of us (T. T. Read) was fortunate enough to obtain, and bring home for study, nine castings, all more than 1000 years old, of which the date of manufacture is precisely known because of inscriptions cast in them, another that lacks a dated inscription, but of which the date, as explained below, can be otherwise established, and a specimen from the largest iron casting ever made,[11] which is also dated. The period covered by this suite of specimens extends from 502 to 1093 A.D. In addition, a sample was obtained from a casting of date unknown, but which was certainly cast before 1000 A.D. and possibly as early as the third century A.D. A detailed description of these specimens is as follows:

1. 502 A.D. A pair (right and left) of recumbent lions (Fig. 1). Base 7¼ by 14⅜ in., height over-all 5½ in., weight 26 lb. each. The translation of the inscription on the base is: "Made on the twenty-fourth day of the seventh month of the third year of Ching Ming of Great Wei" (Sept. 11, 502 A.D.).

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* Metallurgist, with A. W. Deller, Patent Attorney, New York, N. Y.
† Vinton Professor of Mining Engineering, Columbia University, New York., N. Y.
‡ Secretary and Technical Director, Lucius Pitkin & Co., New York, N. Y.
[1] References are at the end of the paper.

2. 508 A.D.   Two cast-iron ink slabs, ⅞ by 4 by 5¾ in., weight 4¼ lb. each. The obverse bears the inscription: "Yung Ping Seven Star Ink Slab."   The reverse shows the constellation of the Great Bear, with the inscription: "Made under the supervision of Yu Jen in the second month of Spring of Ping Shen" (March, 508).

3. 550 A.D.   A standing figure of Kwan Yin, on a 7¼ by 3¼-in. round (lotus) pedestal, the over-all height being 31 in. and the weight 50 lb. (Fig. 1).   The inscription on the front of the base is: "An image respectfully made by Chang Wen for his parents at Cloud Light temple, Bell Rock Mountain, on the twenty-eighth day of the third month of the first year of Tien Pao" (April 30, 550 A.D.).

4. 558 A.D.   Small standing figure of Kwan Yin (Fig. 1) on a rectangular base, the over-all height being 20 in. and the weight 16 lb.   On the reverse of the halo about the head is the inscription: "This iron image was made on the twenty-fifth day of the ninth month of the sixteenth year of Wu Ting (Oct. 22, 558 A.D.) above for the Emperor and after him for the multitude of lives."

4B. 719 A.D.   A panel 18½ in. square showing three figures (Fig. 2), a central Buddha and two attendants, each standing on a lotus pedestal.   Weight 52 lb.   No sample was cut from this specimen, as it was impossible to obtain one without defacing it.   The inscription is: "Made on the ninth day of the third month of the sixth year of Kai Yüan, Great Tang" (April 4, 719 A.D.).

5. 923 A.D.   Two panels (Fig. 2).   One similar in design to 4B is 13¼ by 17½ in. and weighs 25 lb.; the sample is from this one; the other (shown in Fig. 2), with only two standing figures, is 9½ by 19 in. and weighs 25 lb.   Each bears the same inscription: "An image respectfully made by monks of the Old Buddha temple on the ninth day of the tenth month of the second year of Tung Kwang of Great Tang" (Nov. 20, 923 A.D.).

6. 953 A.D.   Sample from 20 by 16-ft. cast-iron lion at Ts'ang-chow.   (See ref. 11 for detailed description.)   An illustration of this appeared in MINING AND METAL-LURGY in August, 1937.

7. 1093.   One of 1024 cast-iron panels, 7¼ by 7¾ in., from a pagoda built at Chü-Yüng (26 miles east of Nanking) in 1093 (Fig. 2).   Weight 6 lb.   The inscription says: "Given by Mrs. Hsü, a female disciple of this province."

8. ? Date.   Sample from "flying scissors." Nanking (Fig. 3.)   Date unknown, certainly earlier than No. 7, and perhaps as early as 300 A.D.

9. ? Date.   Sample from cast-iron stove.[2]   Almost certainly older than 200 A.D.

As nothing has hitherto been published in English about the casting represented by sample No. 8, a brief description seems necessary.   This casting, shaped like an X, 3 by 6 ft., and weighing about 1500 lb., has been described by Louis Gaillard (Variétés Sinologiques, Shanghai, 1904) as well as two other similar ones.   The purpose of all three is completely unknown.   Chinese writings generally ascribe a third century date to one of them, but there is nothing more definite about the one from which the sample was obtained than a remark by a fourteenth century Chinese author, who said it was so old at that time that no one any longer knew when it was made or for what purpose.   It has been included in the suite because of the considerable probability that it represents a date intermediate between No. 1 and No. 9, the latter being the earliest specimen of iron casting so far discovered.   No. 1 is the earliest precisely dated iron casting known to exist.

As to the authenticity of these castings, there can be no doubt as to No. 6, as it was taken by one of us (T. T. Read) and the date cast into the lion is supported by documentary evidence as well. Nor is there
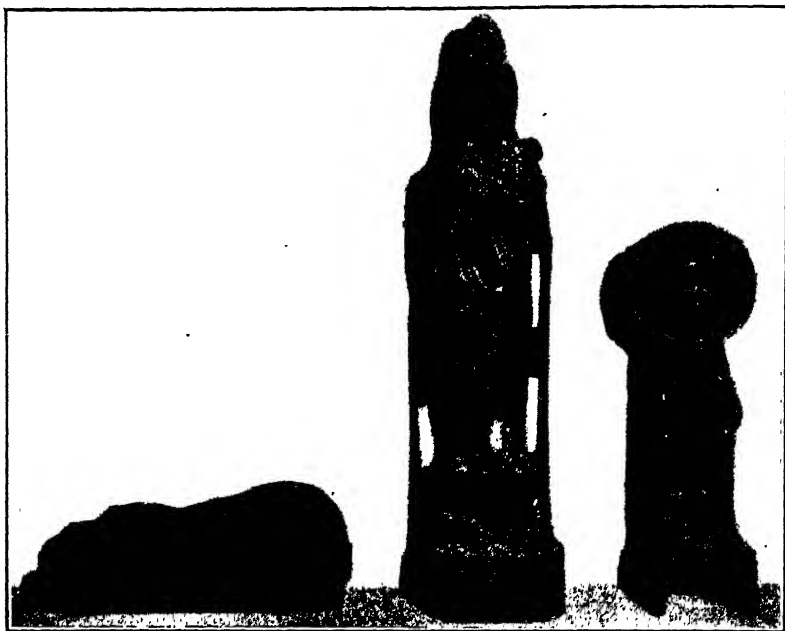
FIG. 1.—LEFT TO RIGHT: No. 1, 502 A.D.; No. 3, 550 A.D.; No. 4, 558 A.D.
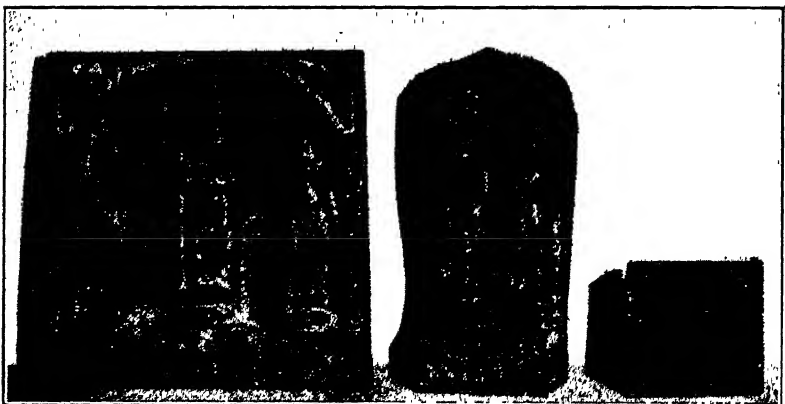
FIG. 2.—LEFT TO RIGHT: No. 4B, 719 A.D.; No. 5, 923 A.D.; No. 7, 1093 A.D.

question as to No. 7, as it was removed from the pagoda under personal supervision. It was evidently built into the pagoda at the time of its original construction, and the date of 1093 A.D. for the latter is amply supported by historical records.

Nos. 1, 2, 3, 4, 4B and 5 have their dates cast in them, and the only question is whether they might possibly be later reproductions of originals that have been lost. The inferences on this point drawn from the analyses and study of the microstructure will be discussed later; it is only necessary to say here that these castings were purchased from curio dealers, or private individuals, in Nanking for prices so small that no one could have made a profit by duplicating an original. The Chinese are not interested in old iron castings, there is no market for them, and where they can be obtained at all it is practically at the price of scrap iron. The inscriptions on Nos. 3, 4, 4B and 5 conclude with two Chinese characters that mean that they were the only pieces cast from that mold.

Without going into further details, we feel confident that these castings are original specimens made at the dates given.

Only No. 3 has in its inscription a place name, and unfortunately it defies identification. It can be merely inference that the castings, obtained at Nanking in 1936, were originally made somewhere near there. The lion at Ts'ang-chow (No. 6) is about 450 miles north of Nanking and was, of course, cast where it now is. Iron would be easily available there from the near-by province of Shantung, which was certainly one of the earliest iron-producing regions of China, a proposal having been made to tax iron there

FIG. 3.—FLYING SCISSORS, NANKING. SPECIMEN No. 8.

in the seventh century B.C. "Buddhist Monuments of China" by Tokiwa and Sekino shows illustrations of cast-iron pagodas, at various places, mostly with tenth and eleventh century dates.

No. 9 came from about 250 miles west of No. 6. The third of the "flying scissors" referred to under No. 8 is at Kian-fu, 425 miles southwest of Nanking, and must have been made locally. This, and other evidence that need not be set forth here, indicates clearly that the casting of iron was an art that was widely practiced throughout China at the time these castings were made. It was an art that was perhaps already at least 1000 years old at the time No. 1 was cast.

Samples were cut from the castings, milled to provide fine cuttings for the analyses, and pieces for polishing and metallographic study produced. Except from Nos. 2 and 4B it was possible to cut fairly large

sections from flanges or other hidden parts without destroying the appearance of the castings. The authenticity of the two specimens numbered 2 was at first doubted and a large segment was cut out of one of the slabs. Both the analysis and the microstructure indicate that these two specimens are also genuine. The results of the chemical analyses are given in Table 1.

TABLE 1.—*Chemical Analyses of Specimens*

Specimen No.	Total Carbon, Per Cent	Combined Carbon, Per Cent	Graphitic Carbon, Per Cent	Silicon, Per Cent	Phosphorus, Per Cent	Sulphur, Per Cent	Manganese, Per Cent
1	3.35	1.05	2.30	2.42	0.205	0.067	0.13
2	3.22	0.96	2.26	2.39	0.17	0.077	0.23
3	3.35	0.33	3.02	1.98	0.312	0.063	0.78
4	3.33	0.16	3.17	2.12	0.186	0.064	0.64
5	3.12	*a*	3.12	2.07	0.297	0.053	0.81
6	3.96	3.35	0.61	0.09	0.231	0.022	*a*
7	3.58	3.54	0.04	0.16	0.134	0.024	0.25
8	3.84	1.49	2.35	0.08	0.097	0.024	0.02
9	*b*	*b*	*b*	*b*	0.124	*b*	*b*

a Not found.   *b* No data.

Spectrographic Analysis

The aim of this was to determine whether germanium, copper, chromium, nickel, antimony and anything unusual was present in these castings. At the same time any major compositional differences, as disclosed by direct arcing in graphite in position 4 of the B. & L. Lithrow spectrograph, covering the spectral range from 2600 to 3800 were to be observed. The procedure was to burn to completion duplicate portions of 50 mg. each, comparing as usual with an ordinary iron as reference. The results were as follows, using the spectral lines as shown in Angstrom Units:

Manganese.—All samples contained manganese (2794.8, 2798.3, 2801.1) in the amount commonly present in ordinary iron, but Nos. 1 and 2 less than Nos. 3, 4 and 5, and Nos. 6 and 8 much less than the others, No. 6 containing the least.

Titanium.—Titanium (2933.06, 3072.92, 3088.03, 3234.52, 3241.989, 3349.44) was present in all samples, but much less present in Nos. 6 and 8. (Note possible interference from iron 3234.621 and silicon 3241.67.)

Copper.—Copper (2824, 3247, 3274) was present in all samples, but No. 6 contained more than the others (estimated as 0.06 per cent).

Magnesium.—Magnesium (2803, 2852) was present in all samples, but much more was present in Nos. 6 and 8 than in the other five.

Germanium.—Samples 1 to 5 inclusive contained a trace of germanium (2651.15, 2651.60), but it was barely discernible in Nos. 6 and 8; i.e., spectrographic traces.

Nickel.—Nickel (3101.6, 3101.9) was not found except in No. 6, which showed a trace estimated as less than 0.004 per cent.

Cobalt.—Cobalt (3044) also was present in No. 6 only.

Silicon.—Silicon (2631.28, 2881.59) was present in all samples, but very much less in Nos. 6 and 8.

Vanadium.—Vanadium (3118.383, 3120.14, 3125.288, 3126.21) was found in all samples.

Chromium.—Chromium (2835.64, 2843.35) was present in all samples.

Aluminum.—Aluminum (3082, 3092) was present in all samples, but more was present in samples 6 and 8 than the others.

Antimony.—Antimony (2877.92, 3029.80, 3232.52, 3267.48) was not found in any samples but is not very sensitive.

Molybdenum.—No evidence of the strongest (10) lines of molybdenum could be found, even in clear regions free of any background.

Tungsten.—No evidence of any tungsten was seen.

Phosphorus.—Phosphorus (2554.9, 2553.3, 2535.6, 2534.0) could not be determined but is given in Table 1. This element is very insensitive in an iron matrix.

The above information has been included in Table 2. This tabulation is a result of some further rechecking with weighted indications of the relative distribution of each element in the various samples. These indications are intended to be read horizontally only and apply only to the respective elements, which should not, therefore, be compared with each other as to amounts present. Arsenic, because of low sensitivity, could not be determined.

TABLE 2.—*Qualitative Spectrographic Estimates*[a]

Sample No.	1	2	3	4	5	6	7	8
Manganese	++	++	{+++ / +++}	{+++ / +++}	{+++ / +++}	+	+++	++
Titanium	+++	+++	+++	+++	+++	+	+++	+
Copper	+	+	+	+	+	++ (0.06%)	+	+
Magnesium	+	+	+	+	+	+++	{+++ / +++}	+++
Germanium	+	+	+	+	+	(+)	+	(+)
Nickel	N.F.[b]	N.F.	N.F.	N.F.	N.F.	(+)	+	N.F.
Cobalt	N.F.	N.F.	N.F.	N.F.	N.F.	++	+	N.F.
Silicon	(Appreciable, ±2%)					+	appr.	+
Vanadium	+	+	+	+	+	+	+	+
Chromium	+	+	+	+	+	+	+	+
Aluminum	+	+	+	+	+	+	+	+
Antimony	Not found in any							
Molybdenum	Not found in any							
Tungsten	Not found in any except No. 7						+	
Tin	N.F.	N.F.	N.F.	N.F.	N.F.	N.F.	{+++ / +++}	N.F.
Silver	N.F.	N.F.	N.F.	N.F.	N.F.	N.F.	+	N.F.

[a] Read for each element alone. Amounts cannot be compared.   [b] Not found.

MICROSCOPIC STUDY

Since each of the castings tended to have a rather uniform cross section, the samples cut from the bases of the hollow castings or from flanges were considered to be representative specimens for microscopic

study. Specimens of the large castings, Nos. 6 and 7, consisted of small fragments about $\frac{1}{2}$ in. in diameter. The other specimens were all taken in cross section.

Polished specimens were prepared and etched with Nital (2 per cent nitric acid in alcohol) to develop the structure. To the eye the polished sections all appeared to be sound, especially Nos. 1 to 5. No. 6 had a mottled appearance, being brightly polished in some portions and much duller in others. No. 8, the least sound, contained several cavities.

Casting No. 1 (502 A.D.).—A cross-sectional specimen taken from the casting was approximately $\frac{1}{4}$ in. thick. Upon examination under the microscope the metal was found to be perfectly sound. It is a gray cast iron with small graphite flakes. The matrix consists of pearlite with occasional patches of the phosphide eutectic. No ferrite was found. Toward the center there were one or two areas rich in this phosphide eutectic. Fig. 4 is typical of the structure except that it shows one of the few high-phosphorus areas, indicated by the white network of the eutectic. The structure at the cast surface was, of course, much finer and had a cellular appearance. Fig. 5 shows the variation in structure from the skin toward the center. Fig. 6, taken near the center of the cross section, shows the details of structure. The matrix is definitely pearlitic in parts.

Casting No. 2 (508 A.D.).—The slab was about $\frac{7}{8}$ in. thick. The metal appeared perfectly sound on microexamination. After etching, the structure at the center was similar to that of the previous one. The graphite flakes tend to be larger, but this is to be expected in a casting of greater cross-sectional thickness. As before, the matrix consisted of pearlite with occasional patches of the phosphide eutectic. Fig. 7 shows the average structure at the center. The coarser graphite occurs in nests. Fig. 8 shows the details of the structure. The cast edge consisted of cells of ferrite and pseudoeutectic graphite surrounded by pearlite and the phosphide eutectic. Fig. 9 shows the structure at the edge, which is indicative of undercooling, or rather, of rapid cooling, but not rapid enough to produce chill.* Superheated metal, when cast, occasionally has this structure. Thin castings may also show it.

Casting No. 3 (550 A.D.).—A cross-sectional specimen, about $\frac{7}{16}$ in. thick, was taken from the base of the casting. The metal appeared sound, except for some rather small cavities near the center. The metal, a gray iron, consisted of very small graphite flakes in a matrix of pearlite, ferrite and the phosphide eutectic, the ferrite tending to occur in patches. There was a perceptible increase in the amount of phosphide eutectic present. The texture of the metal was finer than those previously examined. Fig. 10 shows the structure in depth. At the cast surface are cells of ferrite and pseudoeutectic graphite surrounded by pearlite and the

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* J. W. Bolton: Amer. Foundrymen's Assn. Preprint 37 (1937) 26.

FIG. 4.—No. 1, × 100.   STRUCTURE NEAR CENTER OF CROSS SECTION.
FIG. 5.—No. 1, × 100.   SHOWS VARIATION OF STRUCTURE FROM SKIN TOWARD CENTER.
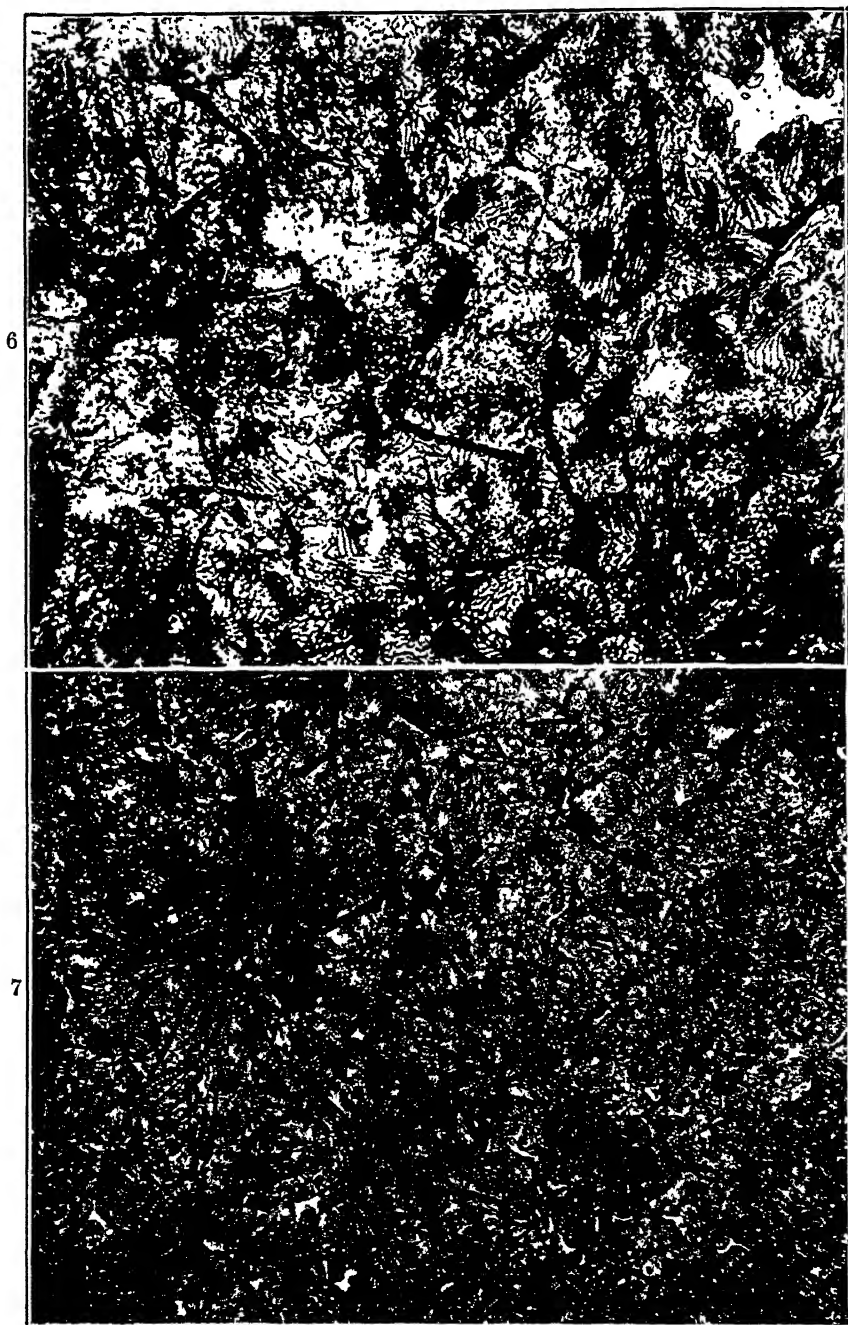
FIG. 6.—No. 1, × 500.   NEAR CENTER OF CROSS SECTION.
FIG. 7.—No. 2, × 100.   AVERAGE STRUCTURE AT CENTER.
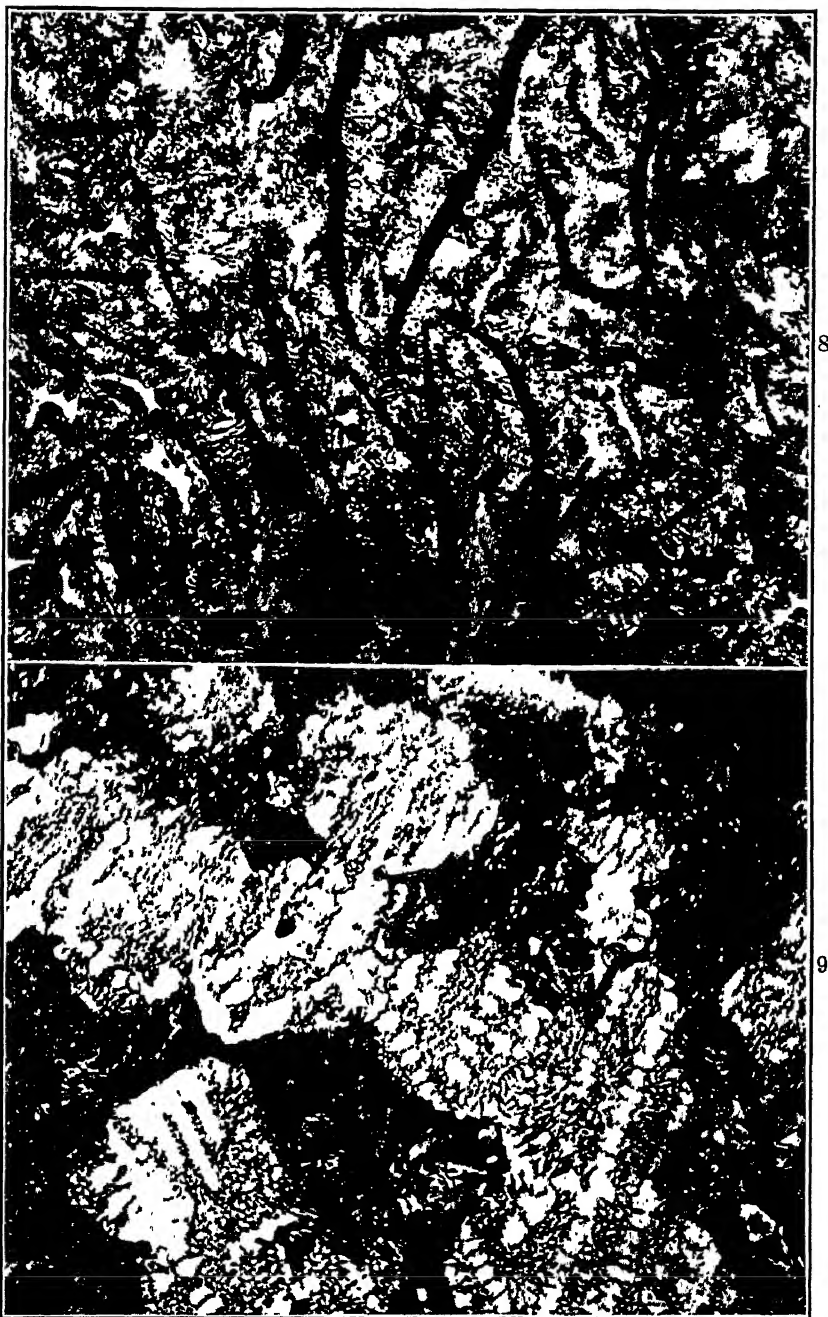
FIG. 8.—No. 2, × 250.   DETAILS OF STRUCTURE.
FIG. 9.—No. 2, × 250.   STRUCTURE AT CAST EDGE.
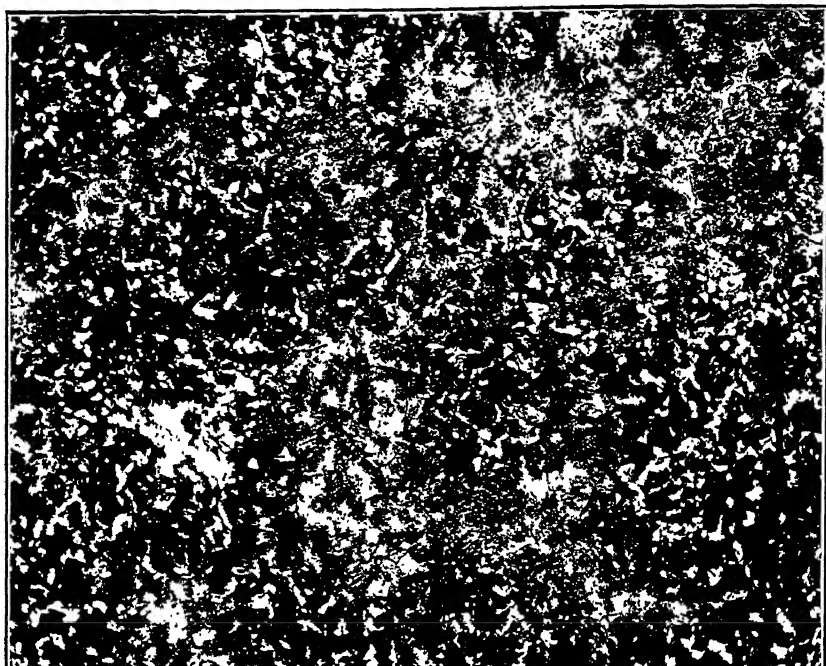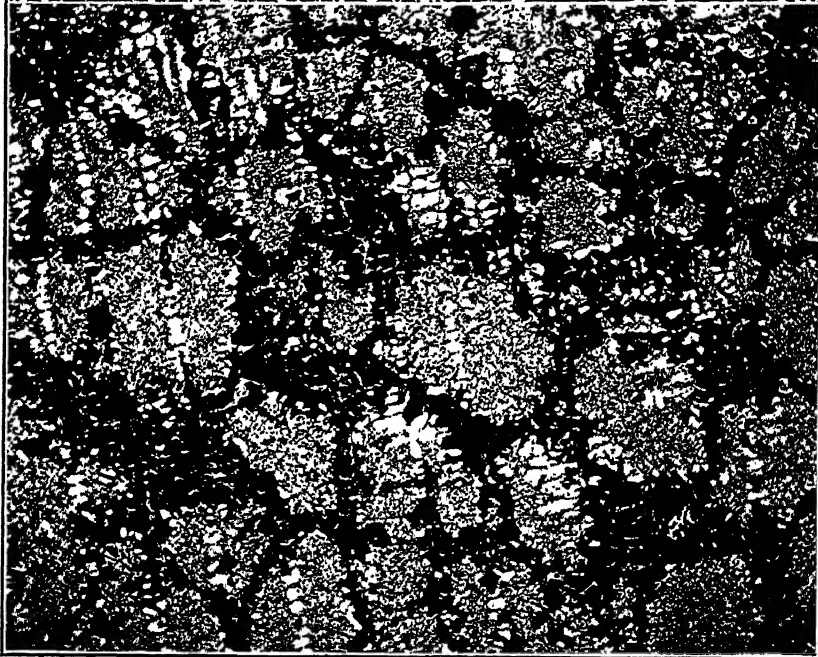
FIG. 10.—No. 3, × 100.   STRUCTURE IN DEPTH.
FIG. 11.—No. 3, × 100.   STRUCTURE OF FIN ON BASE.
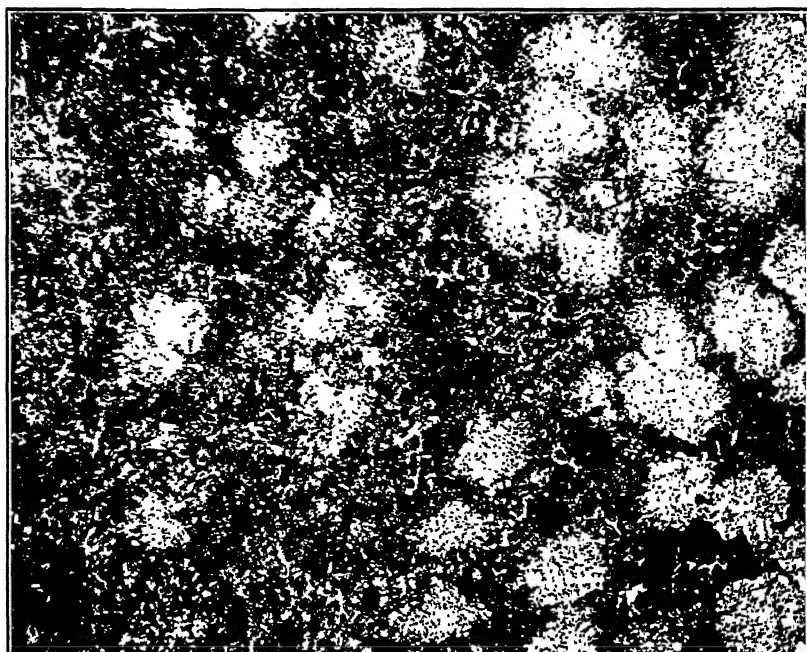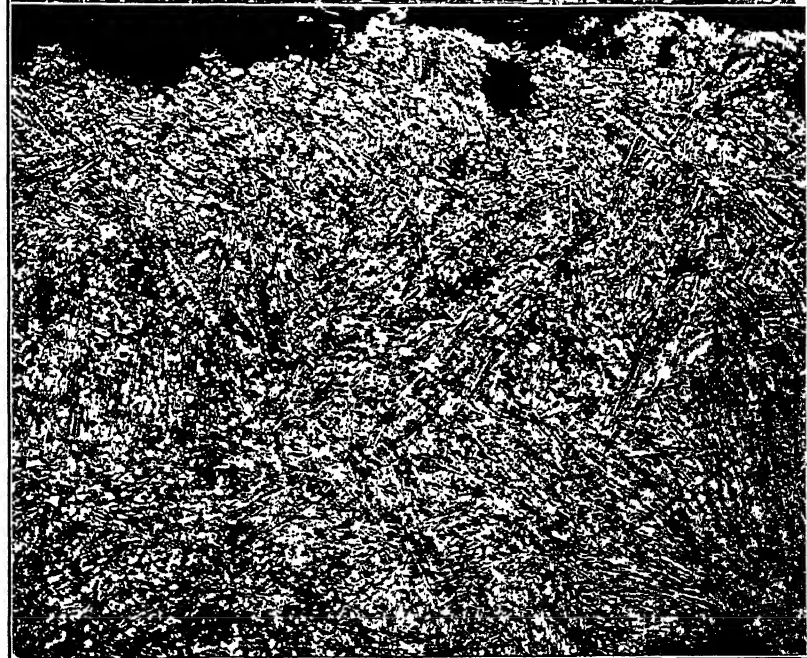
FIG. 12.—No. 4, × 100.   VARIATION IN STRUCTURE FROM SURFACE TOWARD CENTER.
FIG. 13.—No. 4, × 100.   FIN ON BASE, TYPICAL CHILLED STRUCTURE.

phosphide eutectic. This cellular structure, probably indicative of rather rapid cooling, was especially noticeable in a fin on the base of the casting. Fig. 11 shows the structure of this fin and is also characteristic, except for the larger number of cellular patches, of the metal immediately beneath the cast surface.

Casting No. 4 (558 A.D.).—Casting No. 4 has a base about ¼ in. thick. The sound metal, after etching, was rather similar to that found in the previous casting. Fig. 12 shows the variation in structure from the cast surface towards the center. The graphite is very fine. In depth the ferrite loses its cellular appearance and gradually diminishes in amount until it appears as very fine patches and finally disappears near the center. A fin at the base of the casting has the typical structure of chilled cast iron, Fig. 13, merging into the nestlike structure seen in Fig. 12.

Casting No. 5 (923 A.D.).—Two flanges, ⅜ in. thick, formed part of the cast panel. A cross-sectional specimen was taken from one of the flanges. The metal, another gray cast iron, was not quite so sound as that in the previous castings. The graphite is noticeably coarser, and the ferrite, occurring more frequently, appears as nestlike areas throughout the metal (Fig. 14). An appreciable increase in phosphide eutectic is noted. The cast surface was again characterized by a larger amount of the cellular ferritic areas.

Casting No. 6 (953 A.D.).—Whereas the castings so far examined were gray irons, a fragment from the Ts'angchow lion was mainly white iron. It was, for the most part, hypereutectic white cast iron with some mottled iron also present. Fig. 15 shows the typical structure of white cast iron, consisting of excess cementite (the carbide of iron) in the eutectic of iron and iron carbide. The carbon is all in the combined form. This structure is usually found in a very rapidly cooled, low-silicon cast iron. A vein of mottled iron runs through the specimen. Both graphite and undissociated cementite occur in a pearlitic matrix (Fig. 16).

Casting No. 7 (1093 A.D.).—A specimen taken from the flange of the panel, about ¼ in. thick, contained a few very small cavities, but on the whole the metal was sound. The casting was a hypoeutectic white iron, well below the carbon composition of the eutectic. Fig. 17 shows the structure below the surface. The carbon is all in the combined form. (Occasionally some graphite is found.) The structure is pearlite (transformed dendrites of saturated austenite) surrounded by the eutectic (Fig. 18). Throughout the pearlite there are needles of proeutectoid cementite, the result of the decreasing solubility of carbon in austenite below the eutectic temperature.

Casting No. 8.—Date unknown. Earlier than No. 7, and possibly as early as third century. A fragment obtained from the Nanking
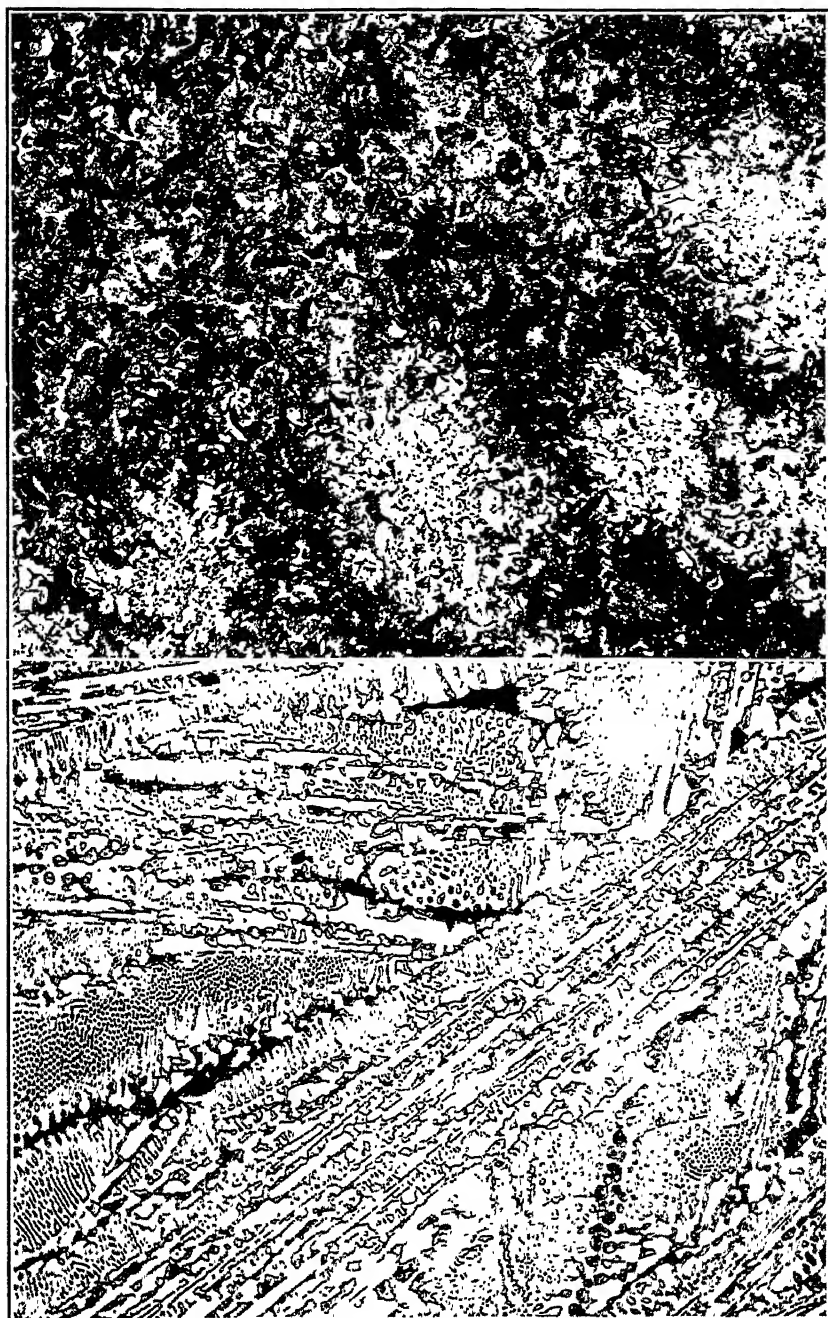
FIG. 14.—No. 5, × 100. CROSS SECTION FROM FLANGE.
FIG. 15.—No. 6, × 100. TYPICAL WHITE CAST IRON.
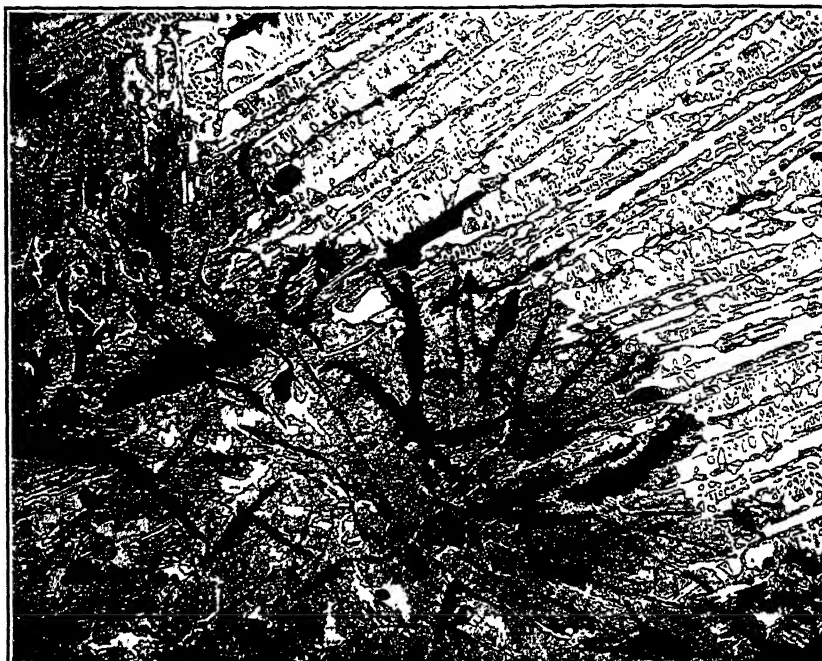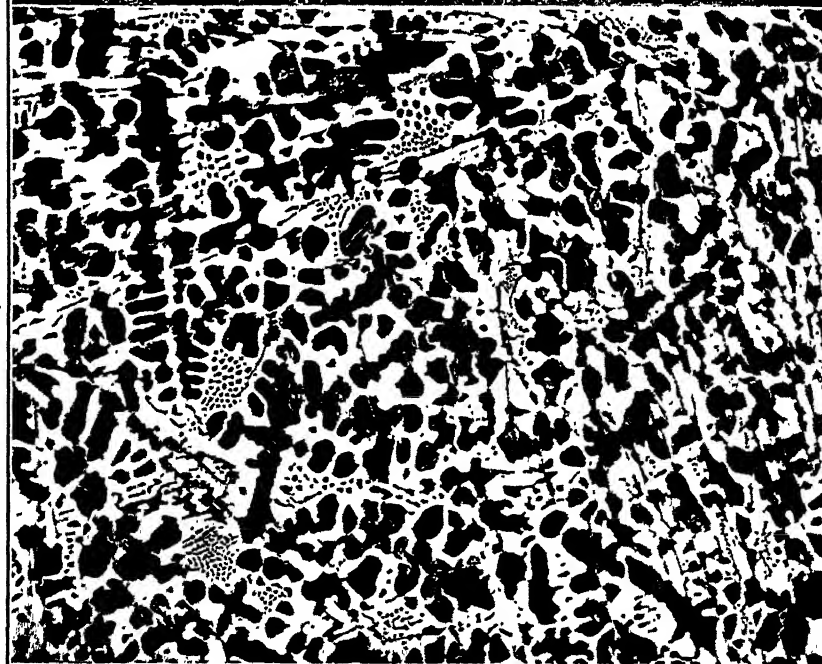
FIG. 16.—No. 6, × 100. LOWER LEFT, VEIN OF MOTTLED IRON.
FIG. 17.—No. 7, × 100. STRUCTURE BELOW SURFACE.

FIG. 18.—No. 7, × 500.   PEARLITE SURROUNDED BY EUTECTIC.
FIG. 19.—No. 8, × 100.   COARSE GRAPHITE AND CARBIDE IN A PEARLITE MATRIX.
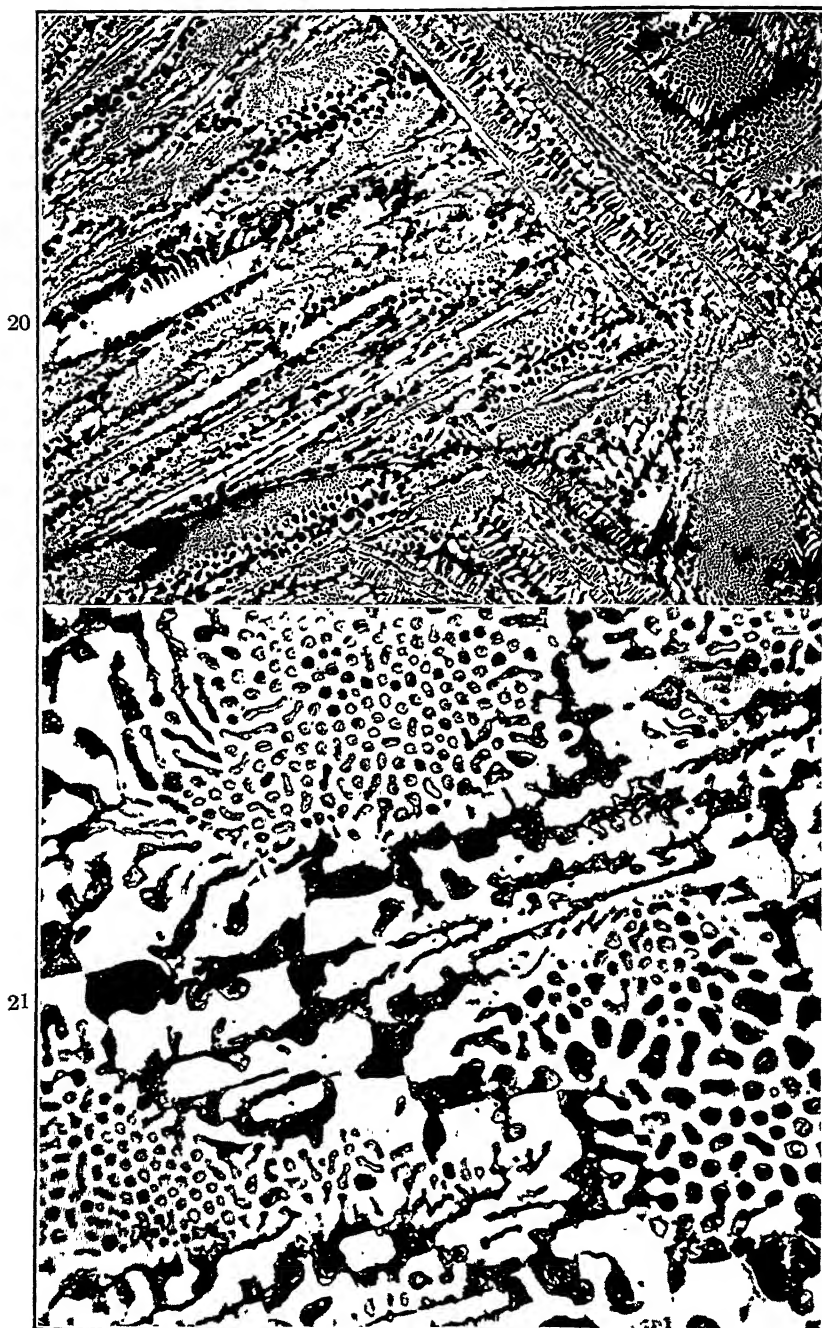
FIG. 20.—No. 9, × 100.   FROM CAST-IRON STOVE.
FIG. 21.—No. 9, × 500.   DETAILS OF STRUCTURE.

"flying scissors" was found to be mottled cast iron. This metal, from a large casting (about 1500 lb.) was the least sound of the suite, containing several cavities much larger than any found in previous specimens. The specimen was taken from a flange on the underside and, as is evident from Fig. 3, the casting has been deeply corroded in places from long exposure in a warm, damp climate. The metal, coarse in structure, consists of graphite and carbide in a pearlitic matrix (Fig. 19). (A few polishing scratches remain because of quick final polishing necessary to retain the graphite.)

Casting No. 9.—Date unknown. Probably before 200 A.D. Through the courtesy of the late Berthold Laufer, who discovered it, a specimen of the metal of a cast-iron stove, dated before 200 A.D., was made available for study. The original is on exhibition in the Field Museum of Natural History, Chicago. The piece examined was about $3_{16}'$ in. thick, and on the inner surface showed an incrustation of iron oxide and more or less friable material that resembled molding sand, but might have been the soil in which the stove was found.* The metal was white cast iron containing plates of excess carbide in the eutectic (Fig. 20). The carbon content was estimated at about 4.5 per cent. Fig. 21 shows the details of structure. The dark etching constituent is assuming the lamellar structure of pearlite. The small size of the specimen available permitted an analysis only for phosphorus, found to be 0.124 per cent.

Summary

The metallographic study of these ancient Chinese castings revealed a wide diversity of structures. White, gray and mottled irons were illustrated. Since most of these castings merely served ornamental purposes, the Chinese were undoubtedly only seeking good impressions. In this connection it is interesting to note the relatively low phosphorus content. One of the authors (M. L. Pinel) had occasion some time ago to examine a Chinese coin of the early eleventh century, which contained 0.52 per cent phosphorus. Another of the authors has reported[1] its present-day use in large amounts in Shansi for the making of thin castings.

Castings 1 to 5 were gray iron, Nos. 1 and 2 being pearlitic and the others containing ferrite in various amounts. The graphite flakes are small and should be expected in thin castings. On the other hand, Nos. 6 to 9 were white or mottled cast irons, Nos. 6 and 9 being somewhat similar except for the presence of some mottled iron areas in No. 6. Whereas the latter were hypereutectic, No. 7 was definitely hypoeutectic. No. 8 was a mottled iron structurally between gray and white irons. The variations in the structure and in the analyses of each of the castings

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* From an unpublished report by William Campbell, No. 1388, Department of Metallurgy, Columbia University, 1932. See reference 2 for the original description of the casting.

tend to confirm their authenticity. In addition, the castings all showed the effects of weathering, particularly Nos. 7 and 4.

Castings 1 to 5, gray irons, were undoubtedly cast in sand molds Most of them tell the exact day of casting and three had cast into them a sign which indicated that only one piece was cast. There would be no need for permanent molds.

No. 7, a small casting similar in size to the gray castings, was one of 1024 such panels. The natural thing in this case would be to use some sort of a permanent mold. The white-iron structure indicates that this is undoubtedly the way in which it was cast. The design would easily permit such practice.

ADDENDUM
By T. T. READ

During the preparation of the foregoing paper questions have been asked that involve the expression of opinions for which my co-authors should not be held in any way responsible. In response to various questions about the making of molds, it may be noted that as early as 1400 B.C. the Chinese were making well designed and perfectly executed bronze castings, 2 or 3 ft. in their greatest dimension. It may be inferred therefore that when they first made iron castings they were competent to do any kind of a molding job that was necessary. I know of no evidence that the Chinese ever used the cire-perdue method for making iron castings. Persons qualified to judge have expressed the opinion, after inspecting the two lions (No. 1, 502 A.D.), that the lower half of the mold was sculptured in the sand without the use of a pattern. Since several of the inscriptions end with two characters that convey the meaning that only one casting was made of that design, this would be a good method whenever it was practicable. But some of the molds were obviously built up by using cores. Terra cotta molds for the casting of coins were commonly used in China at dates earlier than these castings. The British Museum catalogue of Chinese Coins (1892) refers to a cast-iron mold for making brass coins, dated 7 to 22 A.D.

As to the method by which the iron was reduced from the ore, I hesitate to hazard a guess. At one time I felt sure that the Chinese first reduced Fe_2O_3 to Fe, and then melted the particles of metallic iron in a crucible in a blast-blown furnace,[1] but I now feel uncertain whether that method was used elsewhere than in Shansi, and it seems probable that the metal for these castings was produced not far from where they were obtained. Much more research work on the early history of iron in China needs to be done before it will be possible to speak with much confidence on many points.

It is worth noting that the double-acting box bellows used by the Chinese* is an invention of their own, not found elsewhere in the world.

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*See A. P. Hommel: China at work, 18–21.

As a piece of blowing equipment it is much superior to the devices elsewhere used in primitive metallurgical processes, and must have greatly facilitated the melting of metal for casting.

As to the built-up large casting (No. 6) I do not know how the successive layers were made to adhere to each other. The adhesion is far from perfect in places, and deep-seated corrosion has taken place along the joints. As this was merely an art object it was not necessary to obtain strong joints between the successive layers.

The analyses recorded here seem to refute the hypothesis which I suggested in earlier papers, that the Chinese had from very early times added phosphorus to the iron for casting, in order to obtain a more fluid metal; it is not high enough to indicate any deliberate addition. The modern practice of adding it was observed only in Shansi and may be confined to the district where it was seen. It may also be a comparatively late development.

Cast-iron coins have been briefly mentioned in the text above; it may be worth while to record here that there is good evidence that they were made as early as 25 A.D. and were used at various times thereafter. A few hundred yards from No. 6, I saw a fused mass of them (probably resulting from the burning of the temple) that weighed at least several hundred pounds. Only a few were in good enough condition to decipher the characters that indicated their dates. They appeared to be eighth to tenth century.

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DISCUSSION

(George B. Waterhouse presiding)

T. A. WRIGHT.—The part I played in this was very interesting. I am intrigued with the phase of it that had to do with whether one could use a spectrograph for identifying origins or localities from which raw materials come. In other words, the fingerprints, or footprints of nature. I was also interested in improving our knowledge. This work will be looked upon perhaps by some as a very crude spectrographic study, which it is.

Spectroscopists do not know much about examining iron and steel quantitatively as yet. The only people I know of that really have published anything have done an excellent job but their investigations have been limited to several elements at the Campbell-Wyant foundry, under the guidance of University of Michigan men, and deal with a very carefully prepared, chilled cast rod, which avoids segregation as much as possible. One of our problems in this is to derive some true idea as to how representative the results we obtain are, and that point must not be forgotten.

I was interested too in germanium. We were not able to detect arsenic by our method but just as a speculation I wonder does the germanium, or does the arsenic mean anything? It may mean nothing at all, but who dare say so? As regards germanium in iron and steel, I find that many men in the industry do not seem to know that it is presumably more common than has been suspected, but I think that knowledge was first obtained by Meggers at the Bureau of Standards, and he did not publicize it. Two or three years later it appeared in a German publication. I think the Germans felt that the germanium came from the fuel used. I think Dr. Meggers feels, and it sounds reasonable to me, that it may well come from the iron. I have been told that meteorites contain up to as much as 0.5 per cent of that otherwise rare element.

I did notice, aside from No. 6 being different, that, in line with what I said as to origins, No. 7 has tungsten, tin and silver, all of which are not inconsistent with one another, especially the tin and the tungsten on the one hand, or the tin and the silver on the other hand. No. 6 has nickel, cobalt and manganese.

No. 8 was still different as to the low manganese. We put down 2+, a little more than No. 6, and it also differed somewhat in the silicon.

Those were the things that interested me particularly but I would like to leave the thought as to whether some of these elements are additive or counteracting in their effects.

While it is true that it is not wise in a quasiquantitative study to read data such as are given in the paper other than horizontally, yet in a similar study we use a crude numerical index system and dared to add these up for some ten elements. Much to our surprise we obtained a pattern by which we related some six samples of steel to certain differences in a physical characteristic. I may not go more into detail at the moment, for much of a consultant's work is confidential, at least for a period, but determination of the conventionally analyzed allied elements had not disclosed this important and crucial point. Further chemical work has been done, which, based on that, has substantiated it. That simple thing happened previously, in our very early days in working on some white metals. Our experience at that time with those metals did not permit us to be too sure about what we were doing, and yet, by adding up the minor impurities, the bad material was picked out from the good material with one exception in the order of faultiness, if one may use that term, just as in steel. The steel, however, was low carbon, and that is another story from cast iron, of course. I leave the thought.

Distribution of the Metalloids in Rimmed-steel Ingots

By J. W. Halley,* Junior Member, and T. S. Washburn,† Member A.I.M.E.

Rimming steels derive their name from their action during solidification in the molds. As a result of incomplete deoxidation, gas is evolved during freezing, and the metal has a characteristic rolling action. The metal rises along the mold walls and descends in the center of the ingot. This action keeps the top of the ingot open and the advancing rim of solid metal can be seen. The rim grows until the rolling action is insufficient to prevent the top of the ingot from freezing or until the action is stopped by capping the ingot with a heavy plate. The violence of the reaction and its characteristics, such as growth or drop in the molds, are determined by the composition, the furnace practice, and the deoxidation in the ladle and in the molds.

Though rimming steels represent a large proportion of the amount of plain carbon steel made, they have received comparatively little attention in the technical literature. The manufacture of rimming steels has been described by Hibbard,[1,2] Fleming,[3] Pierce[4] and Jackson.[5] The reactions occurring during rimming have been considered from the theoretical point of view by Chipman and Samarin.[7] The structure of rimmed-steel ingots has been discussed by Nead and one of the present authors.[6] Meyer,[8] in studying segregation, investigated the distribution of carbon, sulphur and phosphorus in rimmed-steel ingots by analyzing the rim and core of blooms. In their studies of segregation, the Joint Committee of the Iron and Steel Institute and the British Iron and Steel Federation[9] studied distribution in one billet and one ingot of rimmed steel.

A detailed study of the distribution throughout the ingot has not been published. The present investigation was undertaken to determine accurately the distribution of carbon, manganese and sulphur in normal rimmed ingots and the general distribution of other common elements present. The study included some work on the effect of pouring conditions and furnace practice on the distribution, though there is still much to be done in this direction.

The structure of a rimmed ingot that has been split by dynamiting and a schematic diagram of the zones in the ingot are illustrated in Fig. 1.

The zones differ in structure and composition.   The skin consists of the metal that is chilled by the mold wall.   There are no blowholes in this zone because of its rapid cooling and it has practically the same composition as the liquid metal.   The rim zone consists of the metal that solidifies while the top of the ingot is open and the rolling action is in progress.   It contains lenticular blowholes in the lower portion and consists of purer
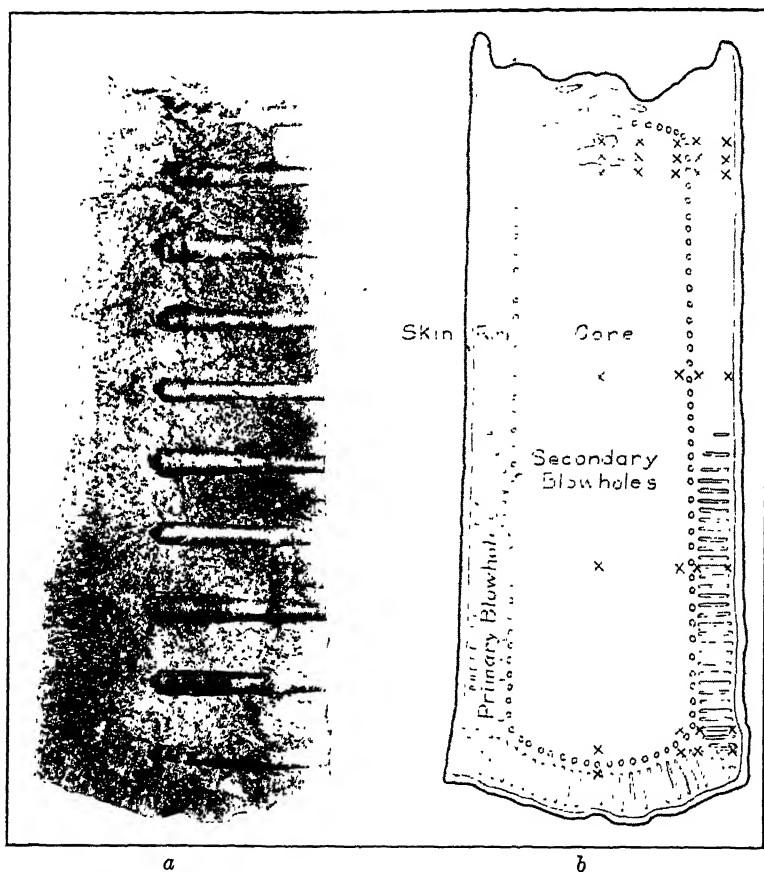
Fig. 1.—Structure of rimmed ingot.
a, ingot split by dynamite; *b*, diagram of zones.

metal than the skin or core.   The blowholes in the rim are called primary because they are the first to form during solidification of the ingot.   The secondary blowholes are formed by the gases that are trapped when the rimming action stops and separate the rim and core.   The core zone consists of the metal that solidifies after the rimming action stops.   The core zone contains scattered blowholes and the least pure metal in the ingot.

This nomenclature was used by Washburn and Nead,[5] and corresponds to common usage except that the "skin" and "rim" are sometimes confused. The confusion results from the appearance of a rolled section of rimmed steel that has been etched on the cross section. The etching shows no distinction between the skin and rim zone but shows a sharp contrast between the rim and core. Usually the same conditions that produce a narrow rim zone also produce a thin skin. This relation has led to the classification of rolled products showing a narrow rim zone on an etched section as "thin-skinned." However, the relationship is not invariably true and a distinction between the skin and rim is necessary.

The following distribution study was made on split ingots. The method of splitting the ingots has been described by Washburn and Nead.[6] The splitting was done by drilling 1⅜-in. holes 6 in. apart along the center of the wide side of the ingot, charging each hole with a stick and a half of 60 per cent gelatin dynamite and firing with electric primers. The holes were drilled slightly over halfway through the ingot. Ingots that had been split to show their structure were drilled for chemical analysis at the points shown by crosses in Fig. 1b. The points for sampling were located so that samples were taken at small intervals where the analysis of the ingot changed rapidly and at larger intervals where there was little change in analysis. Samples were frequently taken between these standard positions to be sure that no discontinuities had been missed. Ingots with a normal structure were found to have quite uniform distribution of constituents.

DISTRIBUTION OF CARBON, MANGANESE AND SULPHUR IN 0.10 PER CENT MAXIMUM CARBON RIMMED STEEL

Figs. 2 to 7 show the distribution of carbon, manganese and sulphur in a normal ingot. The curves represent the change in composition from the bottom to the top, and from edge to center of the ingot. As the distribution is the same on both sides of the center, the curves show the analysis at any point in the ingot. Samples were not taken above 88 per cent of the ingot height because the steel was too porous above this point to give a satisfactory sample for analysis. The curves were obtained by averaging the analyses of ingots from three different heats that showed normal structure and distribution. The average ladle analysis of the heats was as follows: C, 0.09 per cent; Mn, 0.40; P, 0.009; S, 0.025. These ingots were poured 67 in. high in 24 by 43-in. molds.

Fig. 2 shows a model representing the distribution of carbon in a vertical plane from one side to the central axis of the ingot. Sections through the model along the vertical axis of the ingot, and across the ingot at 85, 50 and 10 per cent of the height of the ingot, are shown in Fig. 3. Near the top of the ingot the carbon decreases uniformly from the surface to the secondary blowholes. At the secondary blowholes,

which divide the rim and core zone, there is a sharp increase amounting to 0.04 per cent C. From the secondary-blowhole zone to the center of the ingot the carbon increases comparatively rapidly. At the center
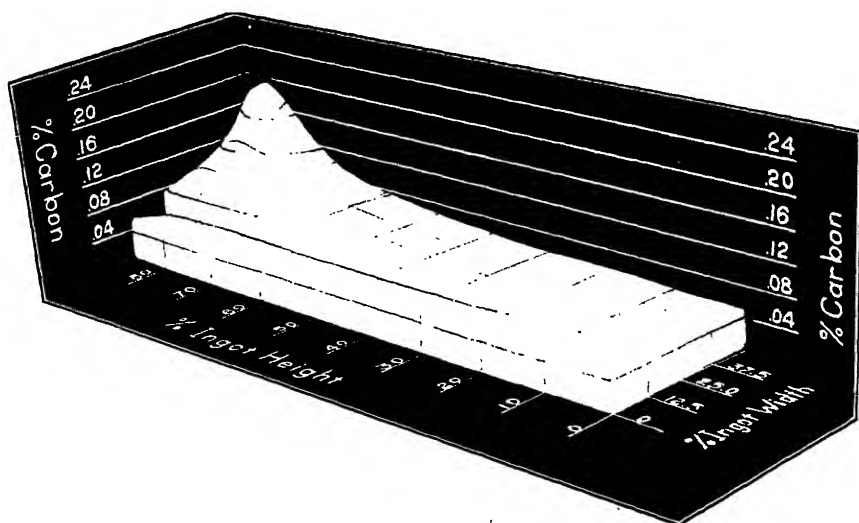
FIG. 2.—DISTRIBUTION OF CARBON IN NORMAL RIMMED INGOT.
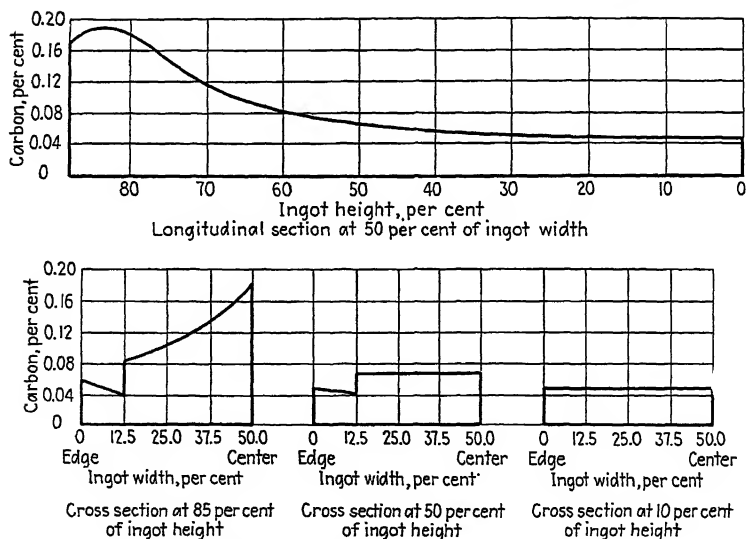
FIG. 3.—SECTIONS OF CARBON-DISTRIBUTION CURVE.

of the ingot and 85 per cent above the bottom of the ingot the carbon reaches a maximum of 0.19 per cent. At half the height of the ingot the carbon is somewhat lower near the surface and decreases slightly through the rim zone. There is an increase of 0.03 per cent at the secondary

blowholes and the concentration of carbon is constant at about 0.07 per cent across the core. At 10 per cent above the bottom of the ingot the concentration of carbon in the steel is uniform across the ingot at about 0.05 per cent C.
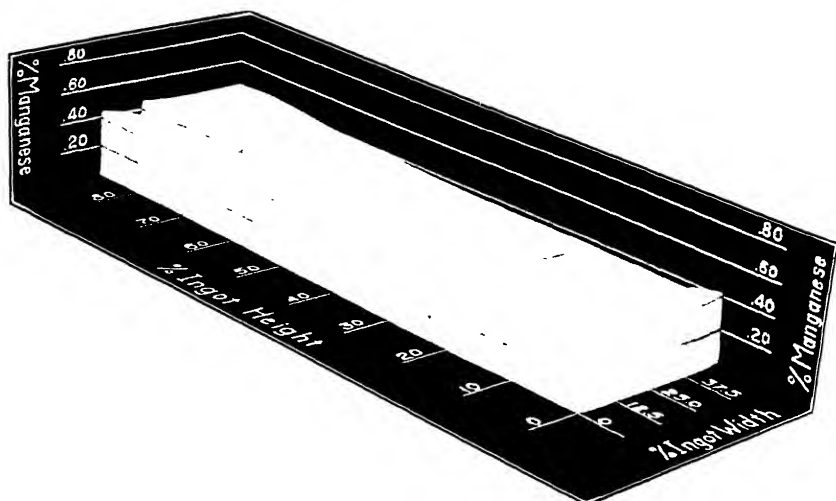
FIG. 4.—DISTRIBUTION OF MANGANESE IN NORMAL RIMMED INGOT.

Longitudinal section at 50 per cent of ingot width

Cross section at 85 per cent of ingot height   Cross section at 50 per cent of ingot height   Cross section at 10 per cent of ingot height
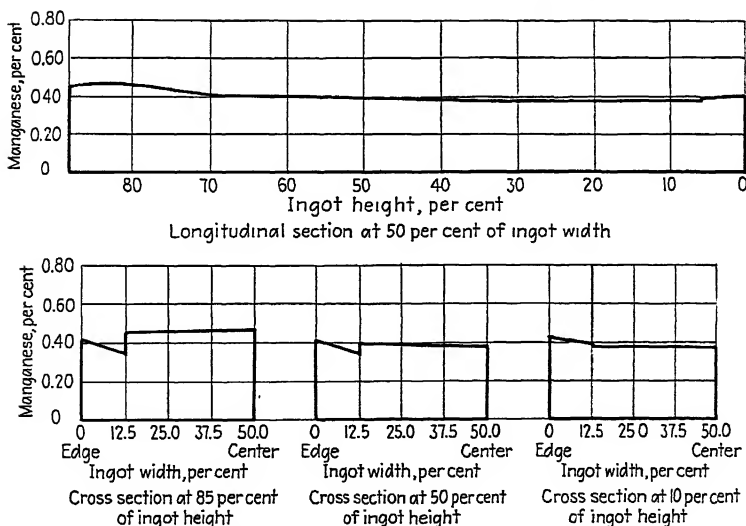
FIG. 5.—SECTIONS OF MANGANESE-DISTRIBUTION CURVE.

A model showing the distribution of manganese is shown in Fig. 4 and sections of the model are shown in Fig. 5. Manganese is distributed much more uniformly through the ingot than carbon. The concentration of manganese decreases from the surface to the secondary blowholes.
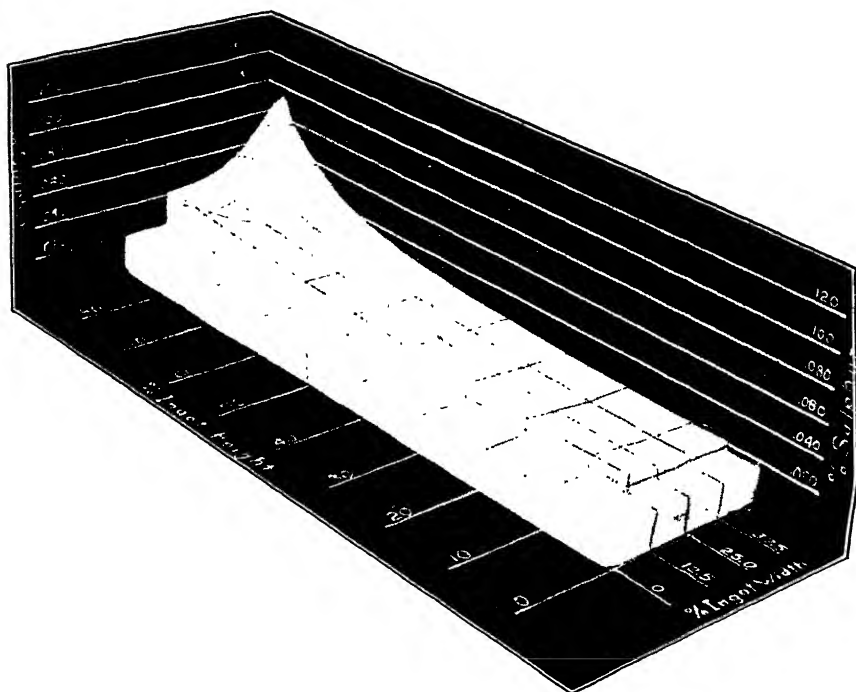
FIG. 6.—DISTRIBUTION OF SULPHUR IN NORMAL RIMMED INGOT.

Longitudinal section at 50 per cent of ingot width

Cross section at 85 per cent   Cross section at 50 per cent   Cross section at 10 per cent
of ingot height   of ingot height   of ingot height
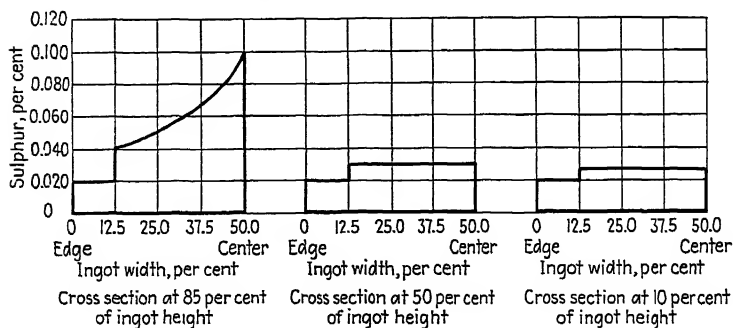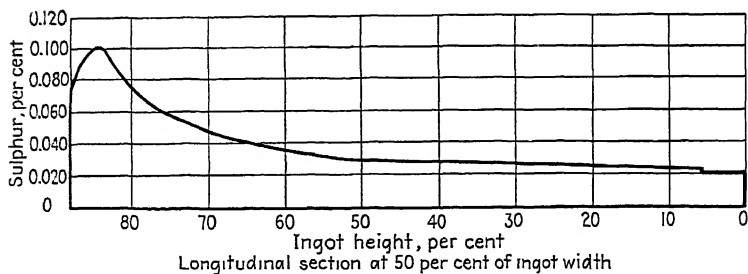
FIG. 7.—SECTIONS OF SULPHUR-DISTRIBUTION CURVE.

This decrease amounts to 0.06 per cent Mn near the top of the ingot and 0.02 per cent at the bottom. At the secondary blowholes there is an increase of 0.09 per cent Mn at 85 per cent of the ingot height, 0.03 per cent at 50 per cent of the ingot height and a decrease of 0.02 per cent near the bottom of the ingot. There is a low-manganese area in the lower portion of the core zone. In this area the manganese concentration is lower than in the adjacent rim zone.

The model representing the distribution of sulphur and the sections of the model are shown in Figs. 6 and 7. The sulphur is approximately uniform in the rim zone at 0.020 per cent. There is a sharp increase at the secondary blowholes, amounting to 0.020 per cent S at the top of the ingot and 0.008 per cent at the bottom. The sulphur reaches a peak at the center of the ingot and at 85 per cent of the ingot height. At this point the steel contains 0.100 per cent S. At 50 per cent of the ingot height the concentration of sulphur is uniform across the core zone, and near the bottom of the ingot the sulphur decreases slightly in the core between the secondary blowholes and the center.

DISTRIBUTION OF PHOSPHORUS, TIN AND COPPER IN RIMMED STEEL

The steel was so low in phosphorus that the usual errors in chemical analysis made it impossible to obtain consistent data for phosphorus distribution. Meyer's[3] results on higher phosphorus steel indicate that the distribution is similar to that of sulphur except that there is less difference between the rim and core and between the top and bottom of the ingot than is shown by sulphur.

TABLE 1.—*Distribution of Tin and Copper in Rimmed Ingots*

Ingot No.	Samples	Percentage of Tin		Percentage of Copper	
		Edge	Center	Edge	Center
1	Top	0.001	0.009	0.04	0.05
	Bottom	0.001	0.001	0.04	0.04
2	Top	0.010	0.024	0.08	0.10
	Bottom	0.010	0.014	0.08	0.08
3	Top	0.022	0.056	0.12	0.11
	Bottom	0.022	0.028	0.12	0.12
4	Top	0.041	0.117	0.15	0.20
	Bottom	0.041	0.056	0.15	0.15
5	Top	0.066	0.157	0.18	0.24
	Bottom	0.066	0.081	0.18	0.18

Some indication of the distribution of tin and copper was obtained on slab tests from ingots to which various amounts of tin and copper had been added. The slabs were drilled for analysis at the center of the core zone and at the center of the rim zone. Samples were taken at the top and at the bottom of the ingot. The analyses for tin and copper are shown in Table 1.

The distribution of tin is similar to that of sulphur but there is less difference in the amount of tin in the low-tin and high-tin areas than in the amount of sulphur. In this respect it is about midway between phosphorus and sulphur. The distribution of copper is similar to that of manganese but it would not be expected to decrease across the rim zone.

FACTORS GOVERNING NORMAL DISTRIBUTION

The marked differences in distribution of carbon, manganese and sulphur indicate different mechanisms controlling the distribution of the three elements. The reaction of carbon with ferrous oxide in the steel is the most important reaction that occurs during rimming and would be expected to control the distribution of carbon in the rim zone. The decrease in carbon across the rim near the top of the ingot indicates that the concentration of ferrous oxide in the liquid steel at the solid liquid interface increases as the rimming proceeds. Near the bottom of the ingot the pressure exerted by the liquid steel is high enough to nearly suppress the reaction between carbon and ferrous oxide. The presence of the primary blowholes indicates that some gas is evolved but the uniform carbon content across the bottom of the ingot shows that little carbon is removed. It is probable that the gas evolution is so slow that the bubbles are trapped between the growing dendrites. In the core zone the distribution is similar to that found in a killed steel and is controlled by the rate of cooling, the distance between the liquidus and solidus of the iron-carbon system, and by the rate of diffusion of carbon in solid iron. The average decrease in carbon between the ladle and the solid ingot is about 0.02 per cent.

The concentration of manganese shows a drop across the rim zone similar to that shown by carbon, which probably is the result of the same change in concentration of ferrous oxide during rimming. As the product of the reaction of manganese and ferrous oxide is a solid rather than a gas, the reaction is affected little by pressure, and the distribution in the rim zone changes little between the top and bottom of the ingot. The manganese oxide formed is carried to the top of the ingot by the rising stream of molten steel and gas during the rimming and combines with ferrous oxide to form the slag found on the top of the ingot. Manganese is also removed with sulphur as manganese sulphide. When the ingot is capped the distribution of manganese is determined by the factors that control distribution in killed steel and by the action of the remaining

manganese oxide. As the particles of manganese oxide have low density, they will rise until the steel in the core zone freezes. This process removes manganese from the bottom of the core zone and results in the low-analysis area shown by the distribution curves.

The distribution of sulphur is not affected by the ferrous oxide content of the molten metal, therefore there is virtually no change in the concentration of sulphur across the rim zone. There is a slight increase in sulphur from the surface to the secondary blowhole zone but this increase amounts to only 0.003 per cent at the top of the ingot and less than 0.001 per cent at the bottom. It is too small to show in the curves but is consistent in ingots from different heats and is probably caused by the increasing sulphur in the molten metal during freezing. The elimination of sulphur from the rim zone is probably largely mechanical. The immiscible manganese sulphide is swept away by the rising stream of gas and molten steel. The distribution of sulphur in the core zone is probably determined by the ejection of manganese sulphide by the freezing steel but the quiet molten metal does not permit the elimination of the manganese sulphide in the same manner as in the rim zone. There is enough progressive concentration to make the last metal that solidifies much higher than the rest of the core. There is some increase in concentration of sulphur toward the top of the ingot resulting from the tendency of the manganese sulphide to rise in the molten steel. The sulphur removal during rimming so overshadows this process that there is no low-sulphur area in the bottom of the core zone similar to that shown by manganese.

EFFECT OF VARIABLES ON DISTRIBUTION IN OPEN-HEARTH PRACTICE

There are so many variables in furnace practice, deoxidation and pouring practice that it is extremely difficult to determine the effect on distribution of any one of the variables. The effect of some changes in practice, such as ingot height, can be determined definitely by varying the practice in different ingots in the same heat. Other factors, such as iron oxide content of the furnace slag, are liable to be overshadowed by other variables and their effect on distribution is very difficult to determine. The factors affecting distribution will be discussed in the order in which their effect can be most definitely determined.

Pouring the ingots higher raises the point of maximum analysis higher in the ingot. An increase of from 67 to 84 in. in ingot height raised the analysis peak from 85 to 88 per cent of the ingot height. In the taller ingots the peak will be sharper and give a higher extreme concentration than in shorter ingots.

Low pouring temperatures give peaks of higher concentration in the distribution curves than high pouring temperatures. With high pouring temperatures there is a sharp drop in carbon and manganese through the

rim from the edge of the ingot to the secondary blowholes. With low pouring temperatures there is little or no drop in analysis across the rim.

Capping the ingot early reduces the width of the rim zone but does not alter the distribution within the rim and core zone. Late capping increases the width of the rim zone and raises the analysis throughout the core zone, but has little effect on the relative distribution within the core zone.

Ingots that rim in flat or rise slightly during rimming have peaks of higher concentration than ingots that drop slightly during rimming.

Heats that are underoxidized in the furnace have very sharp peaks of high concentration and the area of uniform analysis in the core extends high in the ingot.

Summary

The term "normal" has been used with the realization that it applies to only one type of practice and one type of steel and represents a more or less arbitrary selection. However, ingots that showed the greatest departure from normal retained the essential differences in distribution between carbon, manganese and sulphur.

Near the top of the ingot, carbon decreases across the rim, increases sharply at the secondary blowholes and increases from the secondary blowholes to the center of the ingot. At half the height of the ingot the carbon decreases slightly across the rim, increases at the secondary blowholes and is practically constant across the core zone. Near the bottom the carbon is practically uniform across the ingot.

Manganese decreases across the rim zone all the way around the ingot. At the top of the ingot there is an increase in manganese at the secondary blowholes and at the bottom there is a decrease in manganese at the secondary blowholes. In the core zone the manganese increases from the bottom to the top of the ingot but the increase is much smaller than for either carbon or sulphur.

Sulphur is practically constant throughout the rim zone and shows a sharp increase at the secondary-blowhole zone. The increase in sulphur in the core zone between the bottom and top and between the secondary-blowhole zone and the center of the ingot is much greater than the increase in manganese or carbon.

The effects of variation in practice are more indicative than final, and no attempt was made to determine the distribution in different analysis ranges.

his helpful suggestions and criticisms. They are also indebted to Messrs. H. B. Hubbard and A. P. Miller, of the Open Hearth Department, and Mr. H. R. Boatman, of the Metallurgical Department, for their assistance in conducting the experiments.

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DISCUSSION

Evolution of Gases from Rimming-steel Ingots

By K. C. McCutcheon* and John Chipman,† Member A.I.M.E.

To a very large extent the quality of a mild steel ingot is determined by the manner in which it is poured into the ingot mold and its behavior during the first few minutes after it has been poured. The formation of the solid rim of metal around the periphery of the mold, the effervescent action of the liquid steel within this solidified rim and the upward or downward movement of the metal level are indications of what is going on beneath the surface of the liquid metal, especially at the interface at which solidification occurs. Observation of this "rimming action" enables an experienced observer to predict the thickness of the sound skin of the ingot and the location and extent of cavities or "blowholes" caused by entrapment of gases. The control of rimming action at the hands of a skillful steel pourer is a vital part of the control of quality in mild steel sheet, and the behavior of the liquid steel during the rimming period is a useful criterion of the melting and refining practices employed in the open hearth.

The behavior of rimming steel during solidification depends primarily upon the evolution of gases from the molten metal and it is therefore a problem of considerable interest to determine the nature and amount of the gases evolved. A number of attempts to determine either the amount or the analysis of the evolved gases have been reported. Klinger,[1] in 1925, analyzed the gases extracted from rimming, semikilled and killed steel ingots and found that the chief constituent of the rimming gas was carbon monoxide. The relatively large amounts of nitrogen reported in his first few samples may have been due to incomplete removal of air from the gas-collecting mechanism. McKune[2] reported similar studies of rimming ingots from which surprisingly large proportions of nitrogen and hydrogen were evolved. Ameen and Willners[3] determined both the amount and composition of gases extracted from unkilled ingots with the aid of diminished pressure. Their ingots weighed only 80 kg. (176 lb.) and apparently were solid within two or three minutes, so that their

* Assistant General Superintendent, American Rolling Mill Co., Ashland, Ky.
† Professor of Metallurgy, Massachusetts Institute of Technology, Cambridge, Mass.

[1] References are at the end of the paper.

results are entirely inapplicable to studies of rimming behavior of commercial ingots.

METHOD OF COLLECTING GAS

The method used in collecting the gases evolved from an ingot is illustrated in Fig. 1. A sheet-iron hood was made, which fitted loosely into the top of the mold with a clearance 1 in. all around. The hood was of all-welded construction and about 0.12 in. thick. A 1-in. steel pipe was attached. In use the hood was inserted into the mold immediately after filling and forced down into the liquid steel. The delivery pipe was left open to avoid excessive back pressure until the steel between hood
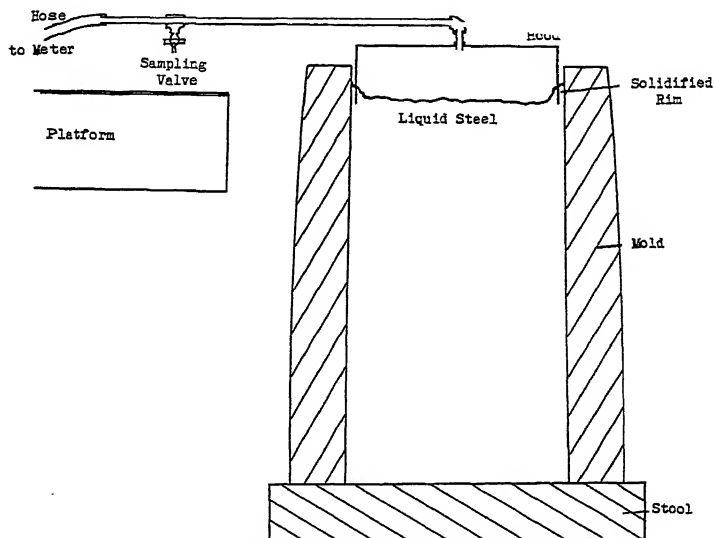
FIG. 1.—METHOD USED FOR COLLECTING GAS.

and mold had completely solidified, which usually required from one to three minutes. When skillfully applied this provided a perfectly gastight enclosure from which air-free samples of gas were obtained, and it permitted a direct measurement of the volume of gas evolved from the time the hood froze in until the ingot had solidified. The gas evolved during filling the mold and the initial stages of solidification could not be measured. All of the results reported in this paper were obtained on 18 by 39-in. ingots weighing 11,300 to 12,000 pounds.

Three methods were employed in measuring the amount of gas evolved. In the early experiments the gas was collected over water, but when it was found that two large oil drums had insufficient capacity for holding all the gas this method was abandoned. An ordinary gas meter such as those used for residence distribution was found to be satisfactory. The total amount was registered on the meter and the rate of evolution

determined by readings at ½-min. intervals. The third method used a differential flow meter having a 0.2-in. orifice in a stainless steel disk with a water manometer connected to either side of the orifice. In order to keep the gas pressure below 15 in. of water a second orifice was used during the period of rapid evolution. Both orifices were calibrated with air, utilizing the flow obtained by displacing air from a large tank with water at a measured rate. In using the orifice meter, the total volume was obtained by graphical integration of the rate curve.
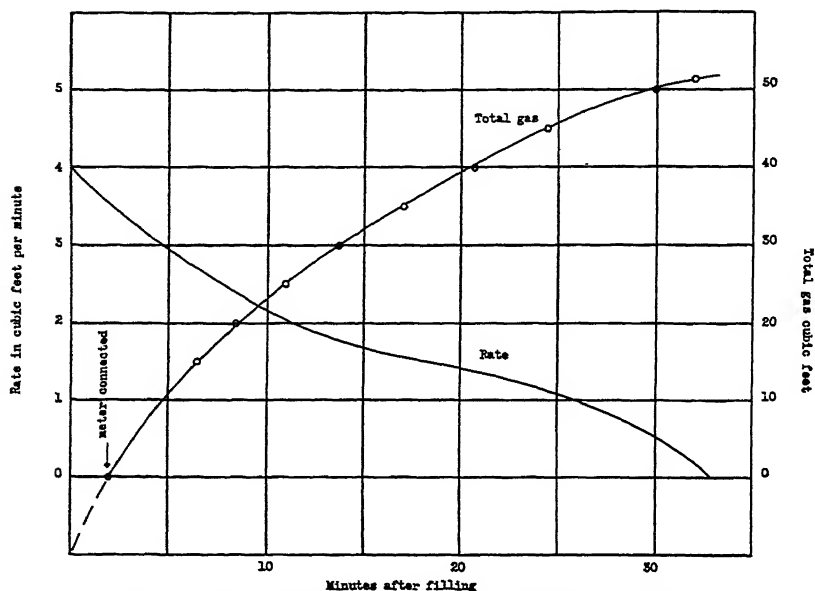
FIG. 2.—GAS EVOLVED FROM INGOT OF 0.073 PER CENT C.

VOLUME OF GAS EVOLVED

A typical result is shown in Fig. 2, in which is plotted the amount of gas evolved from the thirteenth ingot of a heat, of which the ladle analysis was: C, 0.073 per cent; Mn, 0.29; S, 0.023; P, 0.007. Here the meter was connected 2 min. after the ingot was filled. The total amount measured was 52 cu. ft. at 43° C., while perhaps 8 cu. ft. escaped after filling and before the meter was connected. The amount lost during pouring of the 11,500-lb. ingot could not be estimated. The rate curve shown in Fig. 2 was obtained by differentiating the volume curve.

A somewhat slower evolution was found in heats of slightly higher carbon content. Fig. 3 shows the rate of evolution observed with the differential flow meter on the sixth ingot of a heat having the ladle analysis: C, 0.085; Mn, 0.37; S, 0.023; P, 0.007. The integral found by taking the area under this curve indicates a total of 38 cu. ft. at about 20° C. evolved after the time the ingot was filled.

Evolution from a heat of similar analysis measured with the house meter is represented in Fig. 4. The volume measured was 47 cu. ft. at 38° C. and the estimated amount lost before the meter was connected but after the mold had been filled was 7 cu. ft. This was the thirteenth ingot of a heat, having the ladle analysis: C, 0.087; Mn, 0.41; S, 0.018; P, 0.008.

At lower percentages of carbon the amount of gas evolved was slightly greater. Fig. 5 shows the rate of evolution from the seventh ingot of a heat of 0.042 per cent C. Not only is the evolution very rapid at first, but it persists over a long period of time. Integration shows 63 cu. ft. at 10° C. evolved after filling the mold.
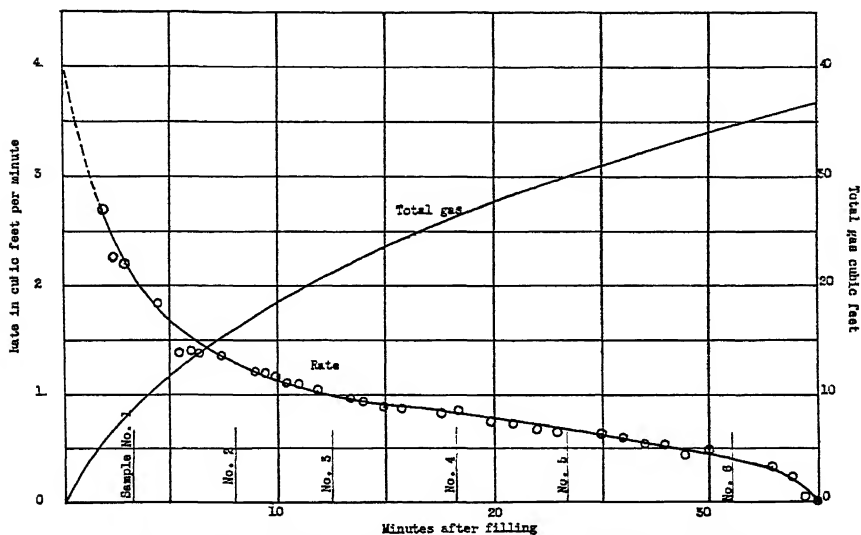
FIG. 3.—RATE OF EVOLUTION FROM INGOT OF 0.085 PER CENT C.

ANALYSIS OF EVOLVED GASES

Gas samples were obtained through the valve indicated in Fig. 1. The samples were collected in all-glass sampling bulbs by displacement of sodium acid sulphate solution. In most of the tests the gas was allowed to flow through the bulb for a short time after all of the solution had drained out, a precaution that minimizes errors arising from differences in solubility among the constituents of the gas. On account of the abundant flow of gas, it was unnecessary to use an aspirator bulb, except in obtaining the last samples from an ingot after the gas flow had practically ceased. The pressure in the collecting system was never reduced below atmospheric and evolution was considered complete when the gas ceased to flow at atmospheric pressure.

The gas samples were analyzed in a modern Burrell analyzer. Transfers and measurements were made over mercury, and absorptions were

carried out by means of the usual reagents, including "cosorbent" for the carbon monoxide. The principal gas was found to be carbon monox-
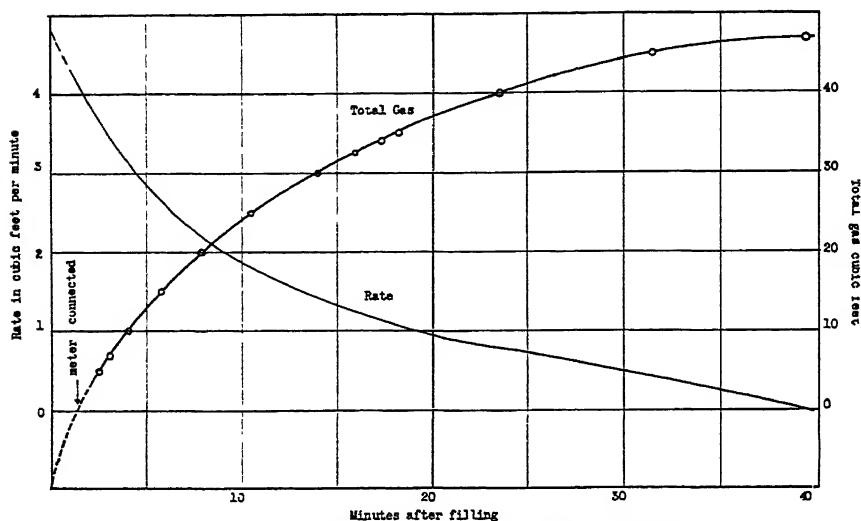
FIG. 4.—EVOLUTION FROM INGOT OF 0.087 PER CENT C.

ide, with which were associated smaller amounts of carbon dioxide, hydrogen and nitrogen. The presence of oxygen in any sample was
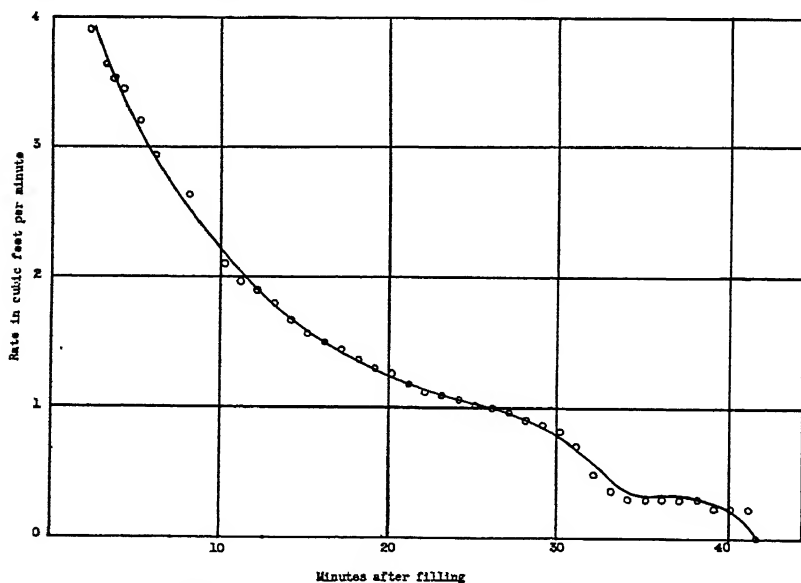
FIG. 5.—RATE OF EVOLUTION FROM INGOT OF 0.042 PER CENT C.

considered evidence of leakage and very few samples showed more than one-tenth of one per cent of this gas. Small amounts of an unidentified

hydrocarbon were found in many of the samples. This was reported as methane, although it was not positively identified.

The results of a series of gas analyses from a typical low-carbon steel ingot are shown in Fig. 6. The data were obtained from the first ingot of a heat of ladle analysis: C, 0.071; Mn, 0.26; S, 0.021; P, 0.007. The analyses show a nearly constant composition of approximately 90 per cent CO, 5 per cent CO_2, 3 per cent H_2 and 2 per cent N_2.

At slightly higher carbon contents the percentage of carbon dioxide becomes smaller and decreases during the period of gas evolution. This is illustrated in Fig. 7, based upon the fourth ingot of a heat having the
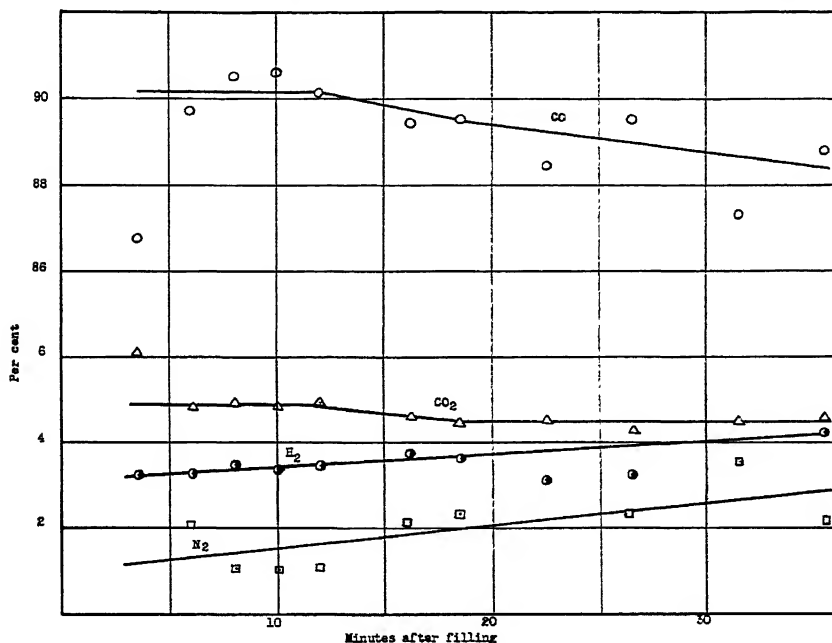
FIG. 6.—COMPOSITION OF GAS FROM INGOT OF 0.071 PER CENT C.

ladle analysis: C, 0.08; Mn, 0.30; S, 0.029; P, 0.008. This plot shows also a gradual increase in the percentage of hydrogen and nitrogen that occurred in the majority of the ingots studied. Another example of the composition of gases from a similar ingot slightly higher in carbon and manganese is shown in Fig. 8—ladle analysis: C, 0.087; Mn, 0.41; S, 0.018; P, 0.008.

A nearly constant gas analysis is shown by the low-carbon copper-bearing steel ingot represented in Fig. 9—ladle analysis: C, 0.062; Mn, 0.25; S, 0.032; P, 0.007, Cu, 0.25. The presence of copper apparently has no effect whatever upon the gas composition. At lower carbon contents, in the range of 0.04 to 0.05 per cent, the carbon dioxide content of the gas is correspondingly increased at the expense of carbon monoxide.
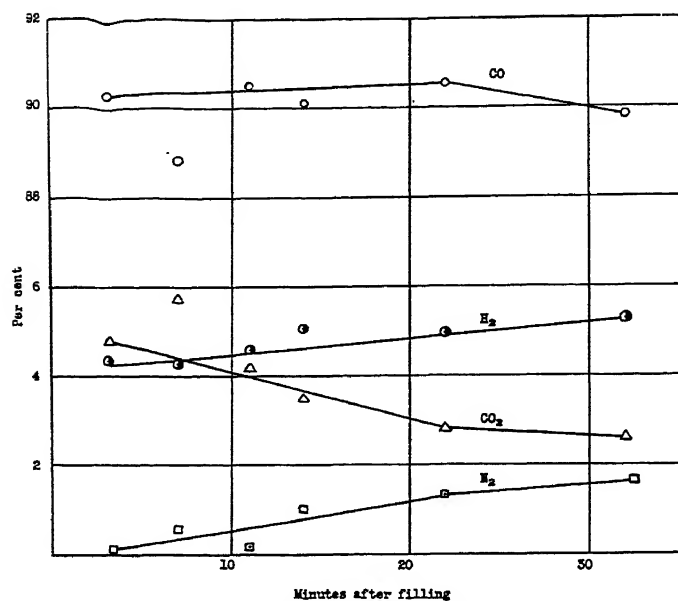
FIG. 7.—COMPOSITION OF GAS FROM INGOT OF 0.08 PER CENT C.
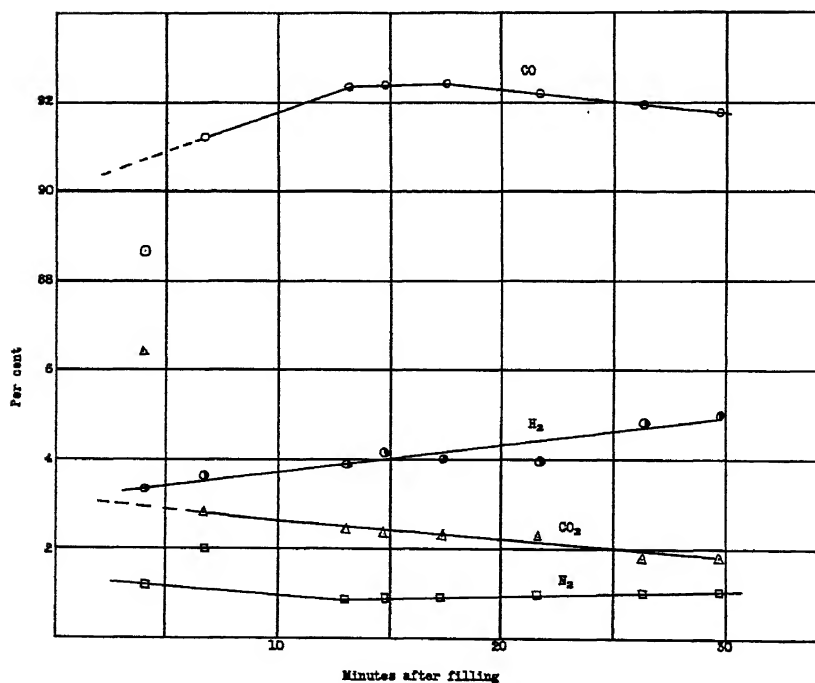
FIG. 8.—COMPOSITION OF GAS FROM INGOT OF 0.087 PER CENT C.
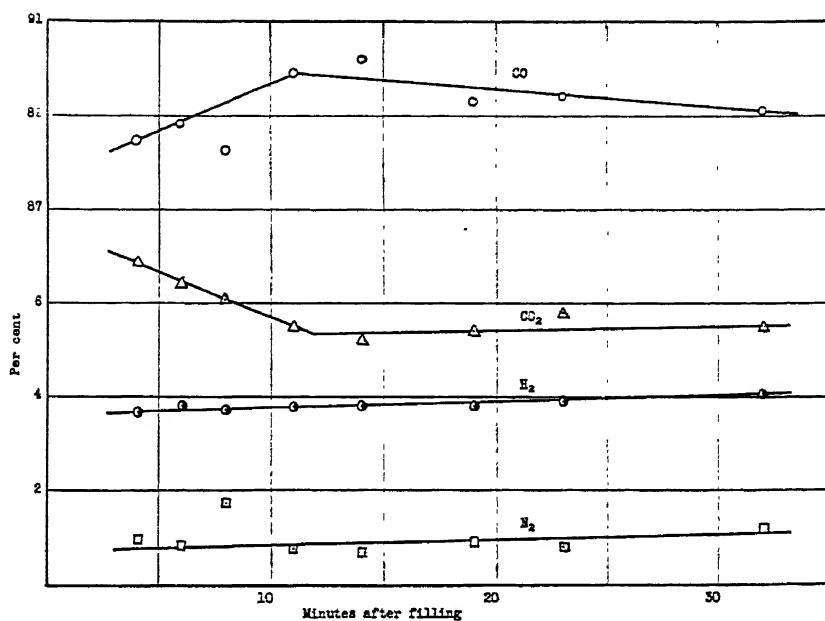
FIG. 9.—GASES FROM COPPER-BEARING STEEL OF 0.062 PER CENT C.
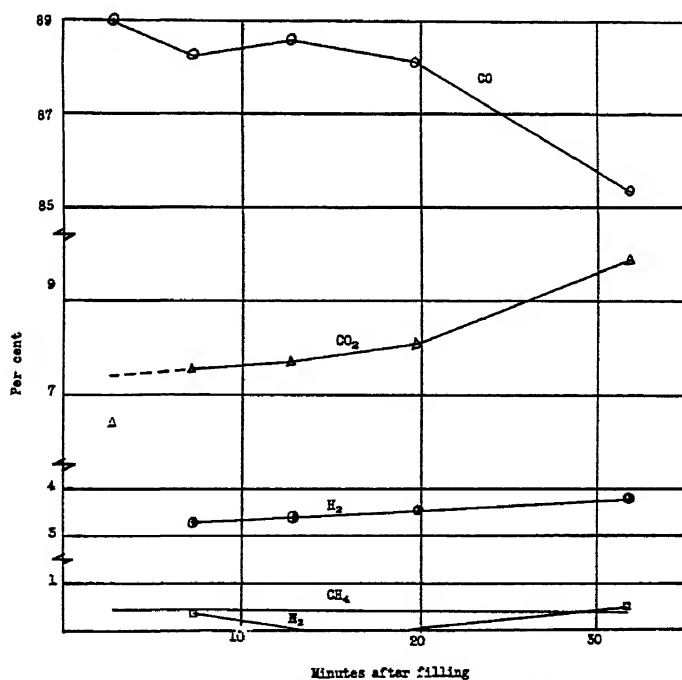
FIG. 10.—COMPOSITION OF GAS FROM INGOT OF 0.042 PER CENT C

Fig. 10 shows the composition of gases evolved from the seventh ingot of a heat in which the metal in the ladle contained 0.042 per cent C. It is noted that in this low-carbon heat there is an increase in the percentage of carbon dioxide toward the end of the evolution period. This is the opposite of the tendency observed in steels of 0.08 to 0.09 per cent C.

SUMMARY OF GAS ANALYSES

During the course of this study, in addition to a number of preliminary trials and unsuccessful attempts, 17 rimming ingots were covered and their gases analyzed. In order to conserve space without omitting the results from any of these ingots, the data are assembled in an abridged form in Table 1. Three or four gas analyses scattered through the evolution period are shown for each ingot. In tabulating the data an attempt has been made to select analyses representative of the much larger total number of analyses obtained and to exclude results involving uncertainties arising from faulty handling or the occurrence of more than 0.2 per cent O_2. The rate data have indicated that at about 7 to 10 min. after the mold is filled one-half of the total gas has been evolved. The analysis of a gas sample during this interval should represent approximately the mean gas analysis for the ingot.

Included in the table is a column showing the duration of the gas evolution. It was noted in general that this is a longer period than an ordinary ingot remains open. The neighboring ingots always solidified across the top before evolution in the covered ingot had ceased. This difference is probably due in large measure to the insulating effect of the hood, which simply causes the surface of the ingot to solidify more slowly.

A column is also included to show the total gas evolved from ingots on which a satisfactory measurement was obtained. This total includes the amount actually measured plus the estimated volume evolved between the completion of pouring and the beginning of the measurement. The uncertainty in this estimate is fairly large. The data provided no basis for estimating the amount of gas evolved while the mold is being filled. This volume has been roughly estimated from the drop in carbon between ladle and mold, and appears to be of the order of 20 to 40 cubic feet.

The effect of carbon content upon both the carbon dioxide and carbon monoxide of the gas is shown in Fig. 11, in which the ratio of the two gases, taken about 8 min. after the filling of each ingot, is plotted against the carbon content of the metal in the ladle. The trend to higher ratios of $CO_2:CO$ at lower carbon content is evident, but no exact quantitative relationship appears. Indeed, no precise relationship of gas composition and ladle carbon is to be expected, since the carbon content of the metal from which the gas is evolved is distinctly lower than that of the metal in the ladle. This will be discussed more fully in a later paragraph.

TABLE 1.—*Summary of Gas Analyses from Each Ingot*

Heat No.	Total Time, Min.	Ladle, Per Cent		Gas, Cu. Ft.	Time after Filling, Min.	Composition, Per Cent				
		C	Mn			CO_2	CO	H_2	N_2	CH_4
1		0 090	0.35		4.6	5.20	88.3	2.75	3.15	0.60
					7.6	4.80	91.4	2.45	0.85	0.40
					12.2	6.85	89.1	2.45	1.00	0.60
2	29+	0.086	0 35		2.2	4.40	89.80	0.65	1.65	3 50
					5.8	4.25	89.55	2.95	2.10	0.15
					9.5	3.45	89.95	3.10	2.90	0.30
					29.2	2.65	89.15	4.40	3.35	0.45
3	34	0.085	0.37		6.5	5.80	89.80	2.95	0.20	1.45
					18.5	5.60	89.40	4.10	0.75	0.15
					30.5	3.20	90.40	4.90	0.85	0.65
4	36	0.070	0.27		4.4	6.20	88.10	1.50	2.10	2.10
					8.4	7.00	87.35	3.30	2.30	0.35
					16.9	5.70	89.30	3.80	2.22	0.00
					35.6	4.20	88.60	3.55	3.45	0.20
5	37	0.071	0.26		3.5	6.10	86.75	3.20	3.80	0.15
					8.0	4.90	90.50	3.45	1.10	0.05
					16.5	4.60	89.40	3.75	2.15	0.10
					35.5	4.60	88.80	4.25	2.15	0.20
6	32+	0.060	0.25		4.0	6.85	88.45	3.65	0.95	0.10
					8.0	6.05	88.25	3.75	1.75	0.10
					14.0	5.20	90.20	3.80	0.70	0.10
					32.0	5.50	89.10	4.05	1.25	0.10
7	39	0.087	0.41	54	4.0	6.40	88.65	3.30	1.20	0.40
					5.5	2.85	91.20	3.60	2.05	0.25
					13.4	2.35	92.40	4.15	0.90	0.15
					28.6	1.80	91.75	5.00	1.05	0.25
8		0.073	0.29	62	6.0	4.35	90.65	4.05	0.80	0.15
					14.0	3.95	90.65	3.85	1.30	0.25
					22.0	3.20	91.60	4.25	0.75	0.10
9	42	0.065	0.26	74	6.5	5.90	90.40	3.55	0.00	0.35
					9.5	4.40	91.90	3.65	0.00	0.05
					16.5	3.95	92.50	3.30	0.20	0.05
					35.5	3.00	91.40	3.85	1.75	0.00
10	27	0.07	0.31	48	3.5	4.67	86.17	5.19	0.97	0.70
					7.3	4.75	87.88	5.32	1.35	0.40
					22.0	3.55	89.42	4.62	1.49	0.82
11	38	0.08	0.30	43	4.0	4.77	90.32	4.31	0.10	0.30
					7.5	5.71	88.83	4.28	0.58	0.50
					15.0	3.48	90.06	5.05	1.01	0.25
					32.0	2.60	89.83	5.31	1.66	0.40
12	29	0.035	0.024	45	2.4	10.25	85.77	2.93	0.28	0.47
					7.0	11.27	83.91	3.86	0.25	0.41
					16.0	12.72	82.20	3.83	0.55	0.40
					24.3	14.81	79.82	3.92	0.55	0.30
13		0.08	0.34		4.0	3.93	90.22	4.77	0.78	0.20
					9.5	7.12	87.08	4.48	0.92	0.30
14	42	0.042	0.021	62	7.3	7.55	88.22	3.29	0.34	0.40
					32.0	9.88	85.33	3.75	0.48	0.35
15	41	0.047	0.030	60	7.8	6.09	89.29	3.46	0.76	0.30
					19.0	6.83	89.35	3.21	0.11	0.40
					37.0	9.81	83.80	3.82	2.12	0.30
16	35	0.085	0.37	38	3.2	3.67	89.20	2.06	2.78	1.61
					7.8	3.67	90.27	4.22	0.87	0.65
					23.2	2.86	88.29	5.85	2.35	0.39
17	35	0.08	0.32	36	9.0	3.78	90.08	4.83	1.05	0.13
					15.5	2.56	89.33	5.53	2.18	0.40
					31.0	1.99	89.01	6.11	2.64	0.25

Some of the results were obtained during the development of the method, before a thoroughly satisfactory system for measuring the rate of evolution had been worked out.   In these instances the volume of gas evolved is not shown in the table; the analytical results are equally as dependable as those on the later heats.   Table 1 includes data obtained in the three open-hearth plants of the American Rolling Mill Co.   Since there were no characteristic differences among the results obtained at the three plants, it is considered unnecessary to distinguish between them in reporting the data.

The effect of pouring too hot was noted in connection with heat No. 13 (Table 1).   The rate of evolution was abnormally slow.   The covered
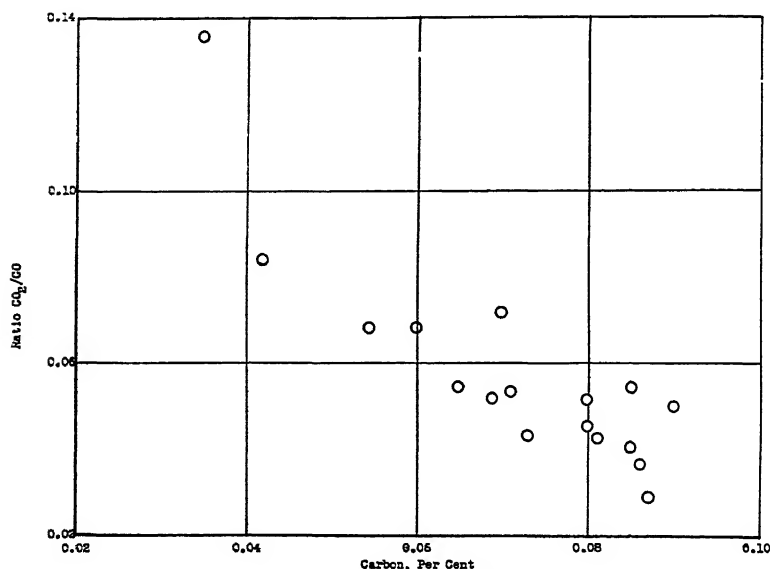
FIG. 11.—EFFECT OF CARBON CONTENT (LADLE) UPON RATIO $CO_2:CO$.

ingot rose enough to fill the hood and shut off the exit tube and the total volume could not be determined.   The gas analysis of the first sample was normal for a heat of this grade but subsequent samples were distinctly higher in carbon dioxide and lower in carbon monoxide.

The effect of a large addition of aluminum during the filling of the mold was investigated in heat No. 9.   It was not possible at the time to obtain a direct comparison with a normal ingot of the same heat but the results may be compared with other measurements on similar heats. The period of evolution was slightly lengthened, especially the interval during which the rate was rapid.   A very slight decrease in rate at the start was more than offset by a sustained increase during the remainder of the period and the net result was an increase in the volume of gas measured.   It seems probable that the amount evolved during the filling

of the mold was decreased and that the effect of the large aluminum addition was simply to delay a part of this loss until later in the evolution period. This observation suggests that the major function of the aluminum addition in rimming steel is to delay, rather than to diminish, the evolution of gas.

COMPOSITION OF LIQUID METAL DURING SOLIDIFICATION

In order to obtain a quantitative relationship between the composition of the metal and that of the gases evolved, it is necessary to have simultaneous samples. Obviously it is not feasible to obtain samples of liquid metal from the ingot that has been covered for the collection of gases, but two adjacent ingots of the same heat are so nearly alike that the same information may be obtained by sampling the next ingot in line. For this purpose a number of sampling cups were made up out of 16-gauge sheet iron, the cups being drawn into cylindrical shape about 2 in. in diameter and 2 in. deep. Each cup was welded to a handle consisting of a 7-ft. length of small steel pipe. To obtain a sample of metal for both carbon and oxygen determination a loose coil of aluminum wire was placed in the cup and the latter was then dipped beneath the surface of metal in the mold, care being taken to avoid the portions of the surface where ingot scum was collecting. The metal contained in the cup was sampled either by drilling from the bottom, the drillings from the cup itself and from metal on the outside being discarded, or by sawing longitudinally and milling the center of the piece. A determination of Al_2O_3 on drillings from the killed sample gives the total oxygen content of the metal. This is an adaptation of the method first proposed by Herty and Gaines[4] for determining the oxygen content of the open-hearth bath.

Since rimming steels are generally treated with small amounts of aluminum in the ladle and in the molds the presence of a little Al_2O_3 in the metal is to be expected. This amount was determined in a number of unkilled samples taken along with the aluminum-killed tests. This alumina was subtracted from the total of the killed sample to obtain that formed from the active oxides in the liquid metals. In a few cases, when no unkilled sample was taken or where an unreliable result was obtained, the correction was estimated from results on other samples. The results of this method of sampling a number of ingots adjacent to those from which gases were collected are shown in Table 2.

The carbon content of the metal in the six ingots from which successive samples were obtained is shown in Fig. 12 as a function of time. The percentage of carbon remaining in the ingot is the resultant of two effects, which exert an opposite influence. First there is a segregation effect, which tends to increase the carbon in the liquid by virtue of the fact that the solid metal formed is more nearly pure iron than the liquid from which it solidifies. Opposing this is the effervescent effect by which

carbon is being constantly eliminated in the form of gas. Each 35 cu. ft. of gas contains 1 lb. of carbon, which is about 0.01 per cent in the ingots used. Fig. 12 shows that at higher carbon contents the two effects very nearly compensate, whereas at lower percentages the effervescent effect predominates and there is a rapid drop in the carbon content of the liquid metal.

The behavior of oxygen is very similar to that of carbon as shown in Fig. 13. The low-oxygen steels lose oxygen while those of higher oxygen content tend constantly to higher levels. Steels of intermediate carbon
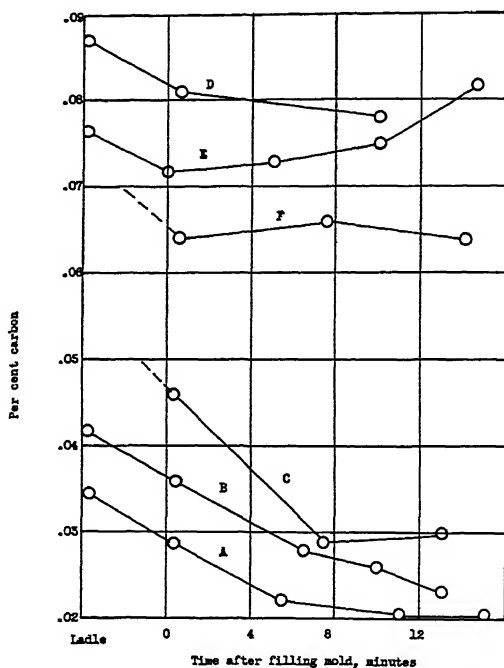
FIG. 12.—CARBON CONTENT OF RESIDUAL LIQUID METAL DURING SOLIDIFICATION OF INGOT.

content, which evolve gas of more nearly constant composition, probably maintain more constant carbon and oxygen concentrations. No dipped samples were secured from this intermediate type.

The last column of Table 2 shows the product of percentage of carbon by percentage of oxygen in the dipped samples. Most of the values of the product lie between 0.0020 and 0.0028. Under equilibrium conditions the value of this product may be obtained from the data of Chipman and Samarin.[5] At 1525° C., the average solidification temperature of the ingots studied, and at one atmosphere partial pressure of carbon monoxide, the equilibrium product is 0.0022. It is significant that, in such a distinctly nonequilibrium process as ingot solidification, the main

chemical reaction of the process can be maintained so nearly at the equilibrium condition. This means, of course, that the carbon-oxygen reaction in liquid steel is a rapid reaction, even when compared with the very rapid process of solidification in a metal mold.

Relation between Gas and Metal Compositions

The composition of the gas issuing from the metal at the time these dipped samples were secured can be obtained by interpolation on the gas-
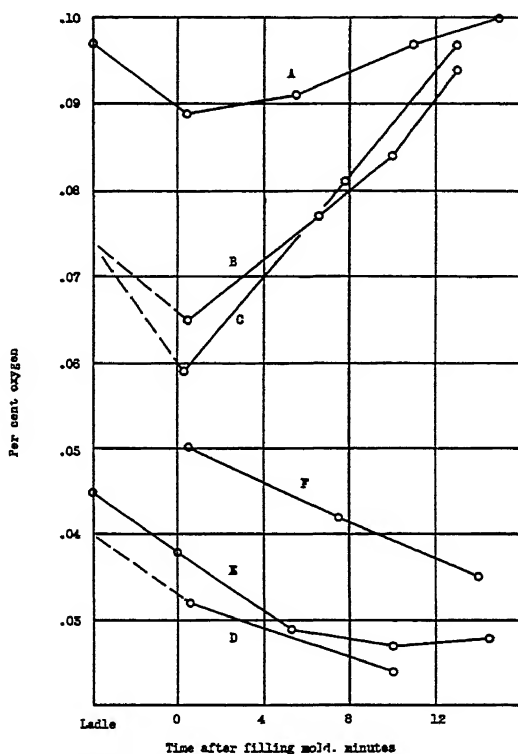
FIG. 13.—OXYGEN CONTENT OF RESIDUAL LIQUID METAL DURING SOLIDIFICATION OF INGOT.

composition curves. In order to estimate the gas analysis at the time the ingot was filled it is necessary to extrapolate back to the zero time axis of the graphs in Figs. 6 to 10. This involves considerable uncertainty, especially in view of the fact that often the first gas sample seems to have been erratic. Errors in the first sample would be expected to be on the side of high carbon dioxide, for two reasons. In sweeping out the last traces of air remaining in the hood, any oxygen present would be converted into carbon dioxide. Any iron oxide, such as rust, adhering to the inside of the hood would be reduced by the carbon monoxide, thus decreastng the percentage of this gas and increasing the percentage of

carbon dioxide.   To avoid this error the covers used on heats 12 to 17 were sandblasted on the inside prior to use, with a resultant improvement in the regularity of the first sample.   The gas compositions as read from the smoothed curves corresponding to each dipped sample are shown in Table 3.

TABLE 2.—*Analysis of Residual Liquid Metal during Solidifying Period*

Heat No.	Sample No.	Time, Min.	C, Per Cent	Oxygen by Al_2O_3 Method, Per Cent			Product Per Cent C × Per Cent O
				Total	As Al_2O_3	Corrected	
12	A-1	0.0	0.029	0.095	0.006	0.089	0.0026
	2	5.5	0.022	0.108	0.017	0.091	0.0020
	3	11.0	0.020	0.106	0.009	0.097	0.0019
	4	15.0	0.020	0.108	0.008	0.100	0.0020
14	B-1	0.5	0.036	0.067	0.002	0.065	0.0023
	2	6.5	0.028	0.080	0.003	0.077	0.0022
	3	10.0	0.026	0.086	0.002	0.084	0.0022
	4	13.0	0.023	0.096	0.002	0.094	0.0022
15	C-1	0.1	0.047	0.061	0.002	0.059	0.0028
	2	7.7	0.029	0.084	0.003	0.081	0.0024
	3	13.0	0.030	0.100	0.018 (?)	0.097	0.0029
7	D-1	0.3	0.081	0.034		0.032	0.0026
	2	10.0	0.078	0.024		0.024	0.0019
11	E-1	0.0	0.072	0.042	0.004	0.038	0.0027
	2	5.0	0.073	0.029		0.029	0.0021
	3	10.0	0.075	0.027	0.000	0.027	0.0020
	4	16.0	0.082	0.028	0.000	0.028	0.0023
13	F-1	0.5	0.064	0.054		0.050	0.0032
	2	5.5	0.066	0.044		0.042	0.0028
	3	14.0	0.064	0.036		0.035	0.0022
	4	22.0	0.065	0.043			
16	G-1	1.0	0.076	0.057	0.012	0.045	0.0034
17	H-1	0.5	0.069	0.051	0.017	0.034	0.0023
	2	10.0	0.060	0.047	0.011	0.036	0.0022

The ratio of carbon dioxide to carbon monoxide in the gas is plotted against the oxygen content of the liquid metal in Fig. 14.   The two straight lines shown on this figure correspond to the equilibrium ratios at 1525° C., the solidification temperature, and 1580°, which is about the highest pouring temperature on any heat.   The majority of the points are within this band, where equilibrium conditions can fully account for the gas composition.   A few points are outside the band, notably samples

TABLE 3.—*Gas Composition Corresponding to Samples Dipped from Ingots*

Heat No.	Sample No.	Time, Min.	Composition, Per Cent		
			CO_2	CO	$\dfrac{CO_2}{CO}$
12	A-1	0.0	9.8	86.0	0.114
	2	5.5	10.9	84.5	0.129
	3	11.0	11.9	83.2	0.143
	4	15.0	12.6	82.4	0.153
14	B-1	0.5	7.3	88.8	0.082
	2	6.5	7.5	88.6	0.085
	3	10.0	7.6	88.5	0 086
	4	13.0	7.9	88.4	0.089
15	C-1	0.1	5.6	90.0	0 062
	2	7.7	6.1	89.9	0.068
	3	13.0	6.4	89.8	0.071
7	D-1	0.3	3.1	90.1	0.034
	2	10.0	2.6	91.8	0.028
11	E-1	0.0	5.1	90.3	0.056
	2	5.0	4.6	90.3	0.051
	3	10.0	4.1	90.4	0.045
	4	16.0	3.4	90.5	0.038
13	F-1	0.5			
	2	5.5	4.1	90.0	0.046
	3	14.0			0.043
16	G-1	1.0	3.9	89.8	0.043
17	H-1	0.5	3.9	89.6	0.044
	2	10.0	3.4	84.6	0.038

B and C, where apparently the composition becomes progressively farther from the equilibrium ratio. It is possible that experimental errors might have been large enough to account for this trend, either in a low reported value for carbon dioxide or in a higher oxygen content in the open ingot, that was sampled than in the covered ingot from which the gases were obtained. Whatever may be the explanation of the apparent anomaly in these two heats, it is nevertheless significant that the gas composition is so nearly that required by equilibrium conditions, and that the deviations are all in the same direction. It can be concluded, from the fact that there are no points on the left of the 1525° line, either that the oxygen content of the metal at the point where the gases are being formed is not higher than that of the bulk of liquid metal from which the samples were obtained or that an adjustment in composition has occurred by reaction

of the gas bubbles with the liquid metal during their rapid rise to the surface. It should be noted that variations in pressure due to ferrostatic head within the ingot have no effect upon the equilibrium involved in Fig. 14. The reaction of these two gases with the carbon of the liquid metal, on the other hand, is greatly dependent upon the pressure and
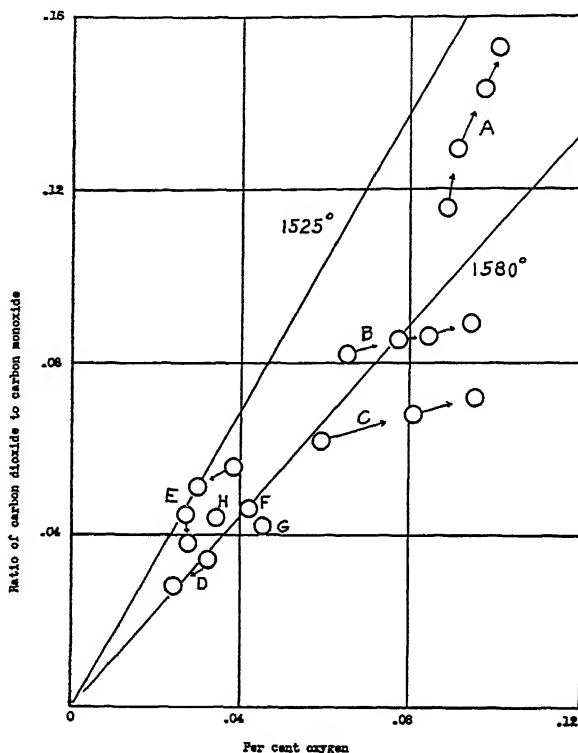
FIG. 14.—EFFECT OF OXYGEN CONTENT OF RESIDUAL LIQUID METAL UPON THE RATIO CO_2:CO IN EVOLVED GASES.

Straight lines represent equilibrium conditions at Centigrade temperature indicated.

cannot be treated mathematically until after we have obtained an estimate of the total pressure at the place where the gases are being formed.

PRESSURE DEVELOPED IN RIMMING INGOTS

The reactions by which carbon monoxide and carbon dioxide are formed, their equilibrium constants and the equations showing the value of these constants at any temperature[5] are shown below:

$$C \text{ (in Fe)} + FeO \text{ (in Fe)} = Fe \text{ (liq.)} + CO; \qquad [1]$$
$$K_1 = (CO)/[(\%C) \times (\%FeO)]; \quad \log K_1 = 2400/T + 0.675$$
$$C \text{ (in Fe)} + 2FeO \text{ (in Fe)} = 2Fe \text{ (liq.)} + CO_2; \qquad [2]$$
$$K_2 = (CO_2)/[(\%C) \times (\%FeO)^2]; \quad \log K_2 = 13,980/T - 6.18$$
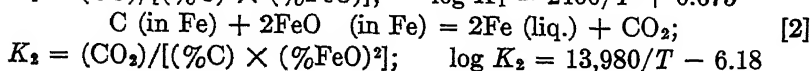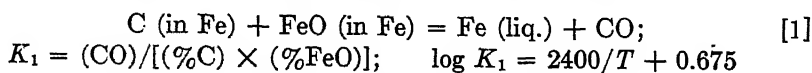
The first of these reactions is only slightly affected by temperature but the temperature coefficient of the second is rather large. This calls attention to our complete lack of information regarding the rate of cooling of the molten metal in the ingot. It has generally been assumed that the temperature of the liquid falls rapidly to the solidification temperature and then remains substantially constant during the remainder of the solidification process. On the other hand, observations on the pouring platform lead to the impression that a rimming heat poured "on the hot side" remains hotter than normal for several minutes after pouring. The temperature at which the actual gas evolution occurs is thus a matter of some uncertainty, but the following computations will be based upon an approximate solidification temperature of steel containing 0.05 to 0.08 per cent C of about 1525° C. The values of the two equilibrium constants at this temperature are: $K_1 = 103$, $K_2 = 40$. For convenience of computation in connection with Table 2, the constants in terms of the percentage of oxygen in the metal are:

$$K_1' = (CO)/[(\%C) \times (\%O)] = 462;$$
$$K_2' = (CO_2)/[(\%C) \times (\%O^2)] = 800$$

The partial pressure of carbon monoxide computed from equation 1, and the carbon and oxygen content of each dipped sample, are shown in Table 4. Similarly, the pressure of carbon dioxide from equation 2 is shown in the fourth column of the table. The partial pressures of nitrogen and hydrogen could likewise be computed from their known solubilities if their percentages in the dipped samples had been determined. This was not done, however, and we may merely note in passing that the percentages of these gases are of the same order of magnitude as we would calculate[5] from their usual occurrence in similar steels. The total pressure, given by the fifth column, is calculated from the sum of the pressures of carbon monoxide and carbon dioxide and the sum of the two percentages as found by analysis. With a few exceptions, there is a certain amount of regularity in these results. The pressure is about 1.4 atmospheres immediately after pouring and gradually diminishes, probably approaching one atmosphere at about the time that evolution ceases.

MECHANISM OF BLOWHOLE FORMATION

The calculated pressures are sufficient to evolve gas under a considerable ferrostatic head. A pressure of 1.4 atmospheres total would correspond to a depth of about 24 in. below the surface of the ingot. This does not mean that no gas can be evolved at a greater depth or that evolution could be suppressed by applying a pressure of 1.4 atmospheres. If evolution were momentarily stopped the carbon and oxygen content of the liquid metal would rapidly increase on account of segregation, so that the gas pressure would soon overcome the external pressure. This is

doubtless exactly what happens in the lower half of the ingot; the gas cannot evolve until the carbon and oxygen percentages have been built up to such amounts that the gas pressure exceeds the sum of the atmospheric and ferrostatic pressures. This occurs only in highly localized positions between the rapidly growing crystals of the solidifying wall, and the result is a honeycomb of long, narrow blowholes. In the upper portion of the ingot, where the gas pressure exceeds the sum of atmospheric and ferrostatic pressure, free evolution of gas occurs and no blowholes are formed, the gas evolution being fast enough to sweep off any bubbles adhering to the solid wall.

TABLE 4.—*Pressure of Gases in Rimming Ingots*

Ingot	Time, Min.	Calculated Pressure, Atmospheres		
		CO	CO_2	Total
A	0.0	1.19	0.18	1.43
	5.5	0.91	0.14	1.10
	11.0	0.87	0.14	1.06
	15.0	0.91	0.16	1.12
B	0.5	1.05	0.12	1.34
	6.5	1.00	0.13	1.17
	10.0	1.00	0.14	1.17
	13.0	1.00	0.16	1.20
C	0.1	1.28	0.13	1.47
	7.7	1.10	0.15	1.31
	13.0	1.32	0.22	1.60
D	0.3	1.20	0.069	1.36
	10.0	0.88	0.038	0.98
E	0.0	1.25	0.085	1.40
	5.0	0.97	0.050	1.07
	10.0	0.92	0.045	1.02
	16.0	1.06	0.053	1.17
F	0.5	1.47	0.13	
	5.5	1.29	0.098	1.48
	14.0	1.02	0.064	
G	1.0	1.57	0.127	1.80
H	0.5	1.06	0.065	1 20
	10.0	1.02	0.065	1.16

At depths where the pressure exceeds that at which free evolution of gas occurs but where it is not great enough to lead to honeycomb formation, an intermediate condition obtains. Owing to the rapid formation

of crystals that are purer than the liquid metal, there is an accumulation of oxygen and carbon in the liquid adjacent to the wall, which gives rise to concentrations appreciably higher than those found in the dipped samples. The gas pressures within this liquid film accordingly will exceed the atmospheric plus ferrostatic pressures at a considerably greater depth than would be calculated from the data of Table 4. The accumulation of these elements depends upon the rate of solidification in such a manner that when solidification is rapid, as during the first one or two minutes after pouring, the gas pressure even at the bottom of the ingot is sufficient for free evolution of gas. As solidification becomes slower, the accumulation becomes less and the honeycomb condition ensues. The fact that the blowholes are nearer the surface in ingots of higher carbon and lower oxygen content[6] implies a more rapid decrease in pressure during the first few minutes after pouring. Similarly, the thin skin of an ingot that is poured too hot indicates a deficiency of gas pressure as compared to a normal ingot, this deficiency being due to the combined effect of slower solidification and lower equilibrium pressures.

In the range of composition under investigation, it has not been possible to differentiate clearly between the effect of carbon and that of manganese, for the reason that in general the higher carbon heats have also contained more manganese. While the major influences upon gas composition appear to be those of carbon and oxygen, it is not unlikely that a part of the differences recorded may have been due to the mild deoxidizing effect of manganese.

SUMMARY

A method is described by which the gases evolved from rimming ingots of commercial size (18 by 39 in.) can be collected for measurement and analysis. This is done by covering the liquid steel in the mold with a welded hood of heavy sheet iron, which is allowed to freeze into the rim of the ingot. The gases are led out through a steel pipe and rubber hose to a gas meter and sampling valve.

The rate of flow was between 2½ and 5 cu. ft. per minute when the meter readings were begun and evolution continued for a period of 30 to 40 min. The total gas evolved after filling the mold ranged from 36 to 74 cu. ft. and it was estimated that between 20 and 40 cu. ft. escaped during teeming. In general, less gas was evolved at 0.09 per cent carbon than at lower percentages.

The gas contained 80 to 92 per cent CO, 2 to 14 per cent CO_2, 2 to 6 per cent H_2, under 3 per cent N_2 and traces of hydrocarbon, persumably methane. As the carbon content increased the ratio of carbon dioxide to carbon monoxide decreased.

Samples from the liquid metal in adjacent ingots were analyzed for carbon and oxygen. It was found that the ratio of CO_2 to CO in the gas was proportional to the oxygen content of the metal, in agreement with

calculations based upon equilibrium conditions. The carbon-oxygen product in the liquid metal was 0.0020 to 0.0028, compared to an equilibrium product of 0.0022 at atmospheric pressure. This was interpreted as indicating that the carbon-oxygen reaction is very rapid.

The gas and metal analyses were used to compute the gas pressure within the ingot, which was found to be about 1.4 atmospheres immediately after pouring. Since the ferrostatic pressure in the lower part of the ingot exceeds this figure, the occurrence of rim blowholes is explained by the inability of localized gas bubbles to grow against the applied pressure. In the upper part of the ingot free evolution occurs and the bubbles are swept away.

ACKNOWLEDGMENTS

Any extensive metallurgical investigation that involves the detailed study of a commercial process requires the cooperation of many individuals. The authors have been fortunate in having the enthusiastic support and assistance of a group without which any such study would have been impossible. This report therefore represents the cooperative effort of this group, for whom the authors are merely acting as spokesmen and scribes.

After many preliminary experiments the first successful measurement of the amount and composition of evolved gas was made by Messrs. William O. Richmond and G. D. Newcomb, at the Ashland plant of the American Rolling Mill Co. Similar measurements at the Middletown and Butler plants were successful through the efforts of Dr. C. D. Foulke and Mr. Shadburn Marshall. To these four, and to Messrs. George M. Coughlin and Frank G. Norris, the authors wish to express their especial thanks. Valuable assistance was also rendered by Messrs. Laurie Rautio, H. P. Gaw, Joe Spang, Homer French and Norman Cox.

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DISCUSSION

[This includes discussion of the paper by J. W. Halley and T. S. Washburn, which begins on page 195.]

(C. H. Herty, Jr. presiding)

T. S. WASHBURN.—When interpreting the analytical results submitted in McCutcheon and Chipman's paper with respect to the type and rate of gas evolution

and the effect on ingot structure during solidification. it would be desirable to keep in mind the role that manganese may play. Because of analytical difficulties. the authors were not able to determine the amount of MnO present and consequently had to report all of the oxygen as in the form of FeO. There will be an equilibrium established between these two oxides, however. depending on the amount of manganese present in the steel. The ratio of MnO to FeO will have an effect on the rate and type of reactions and the temperature at which they occur. therefore this ratio will affect the rimming action and the ingot structure.

E. S. DAVENPORT,[*] Kearny, N. J.—Did Messrs. Washburn and Halley make any attempt, even in a preliminary way, to correlate the occurrence of inclusions in the solid steel with their very interesting results on chemistry? I realize that if they had done any considerable amount of work along this line they would have made some mention of the fact, but I wonder if they have given any thought to that particular phase of the problem.

J. W. HALLEY.—The only thing we have done is some oxide analyses on samples from a slab from the middle of an ingot. The results were not very conclusive but showed more oxides in the core zone than in any other part of the ingot.

J. CHIPMAN.—Mr. Washburn's suggestions regarding the effects of manganese are perfectly sound and very good, I think. We did not find any evidence of an effect of manganese upon the gas composition. In the grades that we used, heats that were higher in manganese were also higher in carbon and the effects of the two elements could not be distinguished experimentally.

The one point of uncertainty regarding manganese is a lack of knowledge of the solubility of manganese oxide in the liquid iron. We know the solubility of FeO accurately. The solubility of MnO is believed to be small compared to that of FeO and this belief is substantiated by experiments of Körber and Oelsen, but exact data are lacking so that it could not be handled quantitatively. On account of this uncertainty all of our analyses are reported as per cent oxygen. not per cent Fe O.

The gas volumes were measured at atmospheric pressure and at the temperature of the pouring platform, which was somewhere between a cold day and a hot day. We did not consider the volumes to be sufficiently accurate to warrant the correction to standard conditions.

C. H. HERTY, JR.,[†] Bethlehem, Pa.—I should like to ask Dr. Chipman a question and point out one thing in connection with his paper. The M.I.T. Practice School, in its station at Lackawanna, has been doing some work with us on gas evolution from rimming steel. We have a little different set-up from Dr. Chipman's; in some ways I think it is better than his and in some ways I think his is the better. We have a special mold with a groove cut into its top, and we slide a hood into the groove so that we are able to get the hood set in 25 sec. after the shutoff. We have greased ways and slide it right on, but the main point of interest to me is this: In every ingot from which we ever took gas samples by simply putting the hood on, measuring pressures, as Dr. Chipman pointed out. we always got rising steel in the ingot. I want to ask Dr. Chipman: Did the steel rise in his hood?

Then, I have a question in regard to whether the molds were tarred. We suspect that a tarred mold or a dry mold has some effect on hydrogen evolved during rimming.

On the plot of CO_2 : CO ratio versus oxygen in the metal, Dr. Chipman, you said they were the same samples, but obviously that could not be true with the hood on. Did you simply spot the CO_2 : CO ratio at equivalent times at which you took pressure?

J. CHIPMAN.—No; obviously, we could not take simultaneous samples. What we did was to sample the next ingot. The samples may have been subject also in the operation to slight atmospheric oxidation, which was absent in the covered ingot. This would account, I think, qualitatively for the fact that the samples were all on the right-hand side of the equilibrium line; that is to say, the reaction may be a little closer to equilibrium than the figure indicated.

We could not see through the hood, to see whether the steel was rising.

C. H. HERTY, JR.—Did you take off the hood?

J. CHIPMAN.—We did in some cases; in others we let it go through the blooming mill.

C. H. HERTY, JR.—A waste of money.

J. CHIPMAN.—In general, where we observed by taking off the hood or watching it through the blooming mills to see what happened, there was evidence that the rimming action went on more or less normally for a little while, and that considerably more rising occurred toward the end of solidification than would occur in an open ingot. The fact that you get 25 per cent more with the aspirator is interesting. We have encountered variations of 25 per cent from one heat to another anyhow, so I think that in order to make an accurate comparison one would have to use adjacent ingots.

We have not attempted to control the pressure other than by designing the meters so as not to put too large a back pressure on the flow of gas. By too large, I mean something of the order of 15 in. of water back pressure. That is a maximum.

The molds in general in our investigation were not tarred. We did have a comparison of two heats, one of which was poured in tarred molds and one in untarred molds, and there was evidence of a little higher hydrogen in the tarred molds; there was also a little more hydrocarbon in that heat. All of these gases contained a little bit of hydrocarbon and we are at a loss to account for its presence. However, it was too small in general to plot, and rather irregular; but in the one test with a tarred mold the gas was a little bit higher in both hydrogen and methane than the corresponding heat.

J. H. NEAD,* East Chicago, Ind.—Dr. Herty, in the tests you carried out at Lackawanna, were the gas analyses similar to those obtained by McCutcheon and Chipman?

C. H. HERTY, JR.—Almost identical.

J. H. NEAD.—Experiments were made along the same line that you described where you put in the top of the mold a number of years ago, but without an aspirator, and no gas was obtained because all the gas went between the mold and the ingot.

C. H. HERTY, JR.—We had the junction of the mold and the stool tightly plugged, so that we got almost identical analyses, but also our volumes just overlapped McCutcheon and Chipman's.

H. J. HAND,† Lorain, Ohio.—On how many heats were those segregation tests run?

J. W. HALLEY.—The particular models were made from three ingots; that is, one ingot from each of three heats. All in all, I think we must have made between 50 and 150, but in a good many of those we were trying to determine the effect of some other

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* Chief Metallurgist, Inland Steel Co.
† Metallurgical Dept., National Tube Co.

variable upon the distribution. The distribution is remarkably uniform on an ingot if it falls within a specified analysis and if the structure is what is considered normal.

We took an average because the heat analyses are not identical, but one could not have recognized the difference by looking at the model of any one of the ingots. Of course, there was a variation among those three in order of 6 to 10 per cent in some points.

H. J. HAND.—I was merely going to suggest that I thought it would prove desirable to conduct a statistical study chiefly through correlation methods between heat history and final segregation result, if the segregation studies were conducted on a number of heats.

J. W. HALLEY.—I think there are possibilities in that.

C. H. HERTY, JR.—I should like to ask a question in regard to the statement that ingots that rim in flat or rise slightly during rimming have peaks of higher concentration than ingots that drop slightly during rimming. Our general experience is that the ingot that falls consistently during rimming will give a higher segregation than the one that rises, which is quite at variance with the conclusion here. How much difference was found in the rising and falling ingots?

J. W. HALLEY.—I do not have the exact figures in mind. I think I have three or four dropping heats. The majority of the heats were flat while two or three were rising heats and the difference was marked. The rising heats showed a very high maximum; sulphur, which shows the greatest variation, was as high as 0.180 per cent.

C. H. HERTY, JR.—Let me ask you just this question, which may be out of order to a certain extent. In the drillings that you took at particular intervals—if you take drillings at a center part of an ingot about 83 per cent and go all the way down to 50 per cent; in other words, take perhaps 15 to 18 drillings to the top of the center of the ingot on the center line—do you find that you get entirely different types of sulphur-distribution curves for various ingots?

J. W. HALLEY.—In many cases we did take samples between the 83 and the 50 per cent position, but we found that the point of maximum analysis always came above 83 per cent. We did not go above 88 because of the many blowholes above this point.

C. O. LARSEN,* Kearny, N. J.—Mr. Halley has indicated that taller ingots give a maximum segregation zone that is higher in concentration and also in position in the ingot. I wonder whether that would also be true of the general pattern of composite segregation; that is, does the general zone of segregation in the upper part of the core tend to approach the top more with the taller ingots—on a percentage scale?

J. W. HALLEY.—Yes.

C. O. LARSEN.—Would the values in the zone below that maximum also be higher?

J. W. HALLEY.—No; in fact, they drop off a little more quickly with a taller ingot. In the taller ingot the concentration will be greater at the 85 or 88 per cent position, but will be lower at the 83 per cent or 70 per cent position than in the normal ingot.

C. H. HERTY, JR.—What do you mean by a taller ingot?

J. W. HALLEY.—The taller ingots were about 78 in. high, compared to 67 in. for a normal ingot.

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* Research Laboratory, U. S. Steel Corporation.

MEMBER.—When you made your comparison between the dropping ingot and the rising ingot did you hold the number of inches from the stool approximately or did you hold a 100 per cent basis?

J. W. HALLEY.—The percentages were taken on the average height of the solid ingot.   On a dropping ingot this would be below the highest point at which the ingot started to freeze and above final height after the ingot had dropped.

C. H. HERTY, JR.—You are talking about a 1 to 2-in. rise and a 1 to 2-in. drop?

J. W. HALLEY.—Yes.

Utility of Statistical Methods in Steel Plants

By H. J. Hand*

(New York Meeting, February, 1938)

Statistical methods are becoming increasingly important for interpreting routine reports, or for analyzing special test data in industrial plants, such as steel plants. They have already become practically a necessity to the plant metallurgist. A paper by Chancellor,[1] written in 1933, gives many examples of the benefits the plant metallurgist can derive from the use of these methods. The present paper discusses applications of importance to many others who must analyze reports in the steel plant, as well as other examples of interest to metallurgists.

Statistical Methods Logically Suited to Plant Problems.—Statistical methods are not new as a branch of mathematics. Until comparatively recently, however, practical applications were confined mainly to actuarial science, biology, and economics; fields in which an observed result is obviously influenced (and often determined) by a complicated set of variables more or less constantly tending to affect it. As pointed out by Daeves,[2] a decade or more ago, problems in industry are basically similar to those in these other fields in that a given result is at least partly due to that chance *combination* of causes *happening* to be present at the time. When trying to do the same thing repeatedly, constant results are never attained; they vary about the desired result with more or less well defined mathematical regularity. Such a condition arises out of the great number of factors tending to affect the final result. If statistical methods are so valuable to the biologist or economist, why then should they not also be of great value to plant managers and engineers, and to all who must interpret reports from various sources in the industrial plant? Within the last few years, industry has become conscious of this situation, and the use of these methods has been rapidly expanding in such plants.†

Many Useful Statistical Devices Available.—Many statistical methods of attack are available for the analysis of plant data. It is the object of

this paper to discuss applications of some of these methods to the solution of problems of diverse nature in a large industrial plant. It is realized that many methods other than those discussed herein can be used for the solution of similar types of problems—in many instances, perhaps, some of these are better fitted for the particular problem on hand than the method selected.*

Scope.—In general, the problems considered in this paper concern:

1. The isolation of factors important as a cause of variability in a given process.

2. Determining whether observed differences between conditions are: (a) due to chance and not likely to be repetitive upon collection of additional data; (b) due to an actual difference between observed differences. Problems of this type for comparing two conditions, as well as those dealing with determining whether sufficient difference exists between a given condition and that which is considered normal to a process, are considered.

3. Methods for determining a direct or indirect effect of one variable affecting a process upon another.

Specific statistical devices utilized are: (1) frequency curves, (2) significance tests for comparing two conditions, (3) control charts, (4) correlation methods.

Utility of Statistical Methods Not Confined to Large Masses of Data.— It is a rather popular fallacy that statistical methods are applicable only when working with large masses of data. While it is true that these methods are very useful in the reduction of large quantities of figures, their application is needed just as much when dealing with small quantities.† Practically everyone who has had to draw conclusions from small-scale experiments has wondered whether the difference between conditions as revealed by the data represents a *real difference*, or is merely the result of *chance factors* and not likely to occur upon repetition of the test. Small sample technique is useful in drawing unbiased conclusions in such cases, it being possible to determine whether the difference is real or due to chance from statistical criteria, based on risk that the observed difference might have arisen from chance alone.

NATURE OF REPEATED OBSERVATIONS OF A CHARACTERISTIC IN INDUSTRY

Frequency Distribution.—As mentioned above, in attempts to produce identical products or attain constant results in industry, sameness rarely results for an appreciable length of time. Instead, products or results distributed with more or less well defined mathematical regularity about

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* It is particularly believed that one method not utilized herein—the Analysis of Variance, extensively developed by R. A. Fisher[4]—would readily lend itself to the solution of many of the problems discussed herein, and to various other problems encountered in industry.

† For a working knowledge of the available methods when dealing with small samples, references 4 and 7 will be found useful.

desired values are invariably obtained. For example, consider the production of steel billets of a certain size from a rolling mill. During the rolling of a considerable tonnage, sizes of calipered billets (one billet calipered per open-hearth heat) are as represented in Fig. 1a. While the specified section has been obtained most frequently, the majority of the calipered billets have actual sizes somewhat higher or lower than that specified, as shown. The mathematical regularity of the increase and then decrease in occurrence, as the size produced increases, results from the numerous factors that are more or less constantly tending to affect cross section in any specific case. The exact size obtained on any billet depends upon the combination of factors that happens to be present at the time. Factors such as the temperature of the steel, shape of the entering bloom, spring and wear of the rolls, analysis of the steel rolled, etc., are all variable, and *always tend* to affect final size. Unless some new factor, such as misalignment of the roll housing, mechanical trouble with the screwdown, etc., enters the system of causes of variability, the final section obtained in a given case depends upon what chance combination of the constantly acting factors happens to be present.

All measurements obtained on materials consumed, on products (chemical or physical, finished or in process), or on indices as to operating conditions (such as yields, defective units, tolerances, costs, or production rates) are similar to the foregoing example in that constancy of results may be desired but never attained. Instead, a *distribution of values* about the desired result (a frequency distribution) is found. All distributions in industry do not have shapes similar to that in the preceding example, however. Examples of a few other types are given (Fig. 1 b–d).

Chance and Nonchance Distributions.—In a study of phenomena wherein the final result is known to be due to chance alone, distributions of shapes similar to many encountered in industry are found. Consider the examples of Figs. 1a and 1b, for instance. In the former figure, superimposed on the curve for actual sizes obtained while rolling billets of a specified section, is a curve showing the chance of obtaining various numbers of heads when tossing 17 coins simultaneously. In the latter figure, a curve is shown for the chance of obtaining various numbers of red balls when drawing 100 balls (with replacement after each draw) from a thoroughly mixed lot of 76 red and 9924 white balls. This curve is superimposed upon one for defective units in a product with low average rejects. Notice how similar the curves depicting performance in an industrial process are to the distributions known to have resulted from chance alone. Although it cannot be determined from casual inspection whether a distribution is chance or otherwise, statistical technique* indicated that

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* Although it cannot be determined that a distribution is chance or otherwise from a casual inspection of the frequency curve, many statistical tests are available that enable this distinction to be drawn. Among these might be mentioned the control-chart method (referred to subsequently), and the χ^2 test.[7]

a AND *b*, PURE CHANCE DISTRIBUTIONS

a.—Sizes of billets obtained when making a specified section.

b.—Rejects in batches of finished tubular product with low average rejects.

c AND *d*, NONCHANCE DISTRIBUTIONS

c.—Hourly rate of production while making a given type of product.

d.—Physical property in heats of a grade of open-hearth steel.

FIG. 1.—EXAMPLES OF FREQUENCY DISTRIBUTIONS ENCOUNTERED IN INDUSTRY.

in both of these examples chance alone was operative. It is thus seen that at least some of the frequencies encountered in industry follow chance laws.

It is interesting, in this connection, that lost-time accidents expressed as a rate *per man-hour of exposure* follow laws of chance very closely for considerable time periods. In fact, the accident curve might well be substituted for that showing the distribution of defects from a lot with low average rejects in Fig. 1*b*, without detracting from the agreement between the actual and the theoretical curves.

In such accidents (just as when tossing coins, drawing balls or rolling dice), chance completely determines the final results, and in any specific case the result obtained is entirely due to the chance combination of influencing factors occurring. Considerable variability in results must be expected, and in future observations conditions should be considered normal if well defined proportions of the observations are found within various limits. Unless conditions change, past records may be used to determine the proportion of observations to be expected within various limits. Frequency curves of this type are known as probability distributions, and the observed result is said to be "statistically controlled."

If it is found that results are "statistically controlled," and extreme values are objectionable, it is just as futile to attempt to isolate specific causes for the occurrence of these extremes as it would be to try to determine why two aces appeared in a given roll with two dice. If results obtained are unsatisfactory, a *fundamental* change must be made in the process that alters the distribution of results.

All measurements obtained in industry, however, do not follow laws of chance. Certain factors, known as "assignable causes of variation," may temporarily enter the cause system determining observed results. Two or more constant acting systems of causes may be present, in which variability is the result of many minor factors, plus that due to two or more major variables differing in their fundamental effect. Examples of these are shown in Figs. 1*c* and 1*d*, the former figure giving the hourly rate of production when making a given type of product while the latter shows the distribution of a physical property obtained on a certain grade of steel. In the former, assignable causes found operating were: (1) starting on a new "run" of the size represented, (2) sticking of pieces in mechanical devices, (3) defective raw materials and (4) crew personnel. In the latter, the modes* were associated with the manner of making the various heats of steel involved. In such cases, where assignable factors operate, the proportion of observations to be expected within various limits cannot be based on past performance in a reliable manner. It could not be said, from the production-rate data, for example, that a

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* A knowledge of statistical terminology is assumed. The reader will find reference 8 very useful in describing the foregoing.

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* A knowledge of statistical terminology is assumed. The reader will find reference 8 very useful in describing the foregoing.

confined range of production could be expected per hour in a given percentage of cases. Presence of assignable causes precludes this deduction. Further, extremes can readily be avoided by eliminating the assignable causes. By eliminating factors that are conducive to low production, the process represented in Fig. 1c will become correspondingly more efficient.

NEED FOR PROPER CLASSIFICATION WHEN ANALYZING DATA

Before discussing how many industrial problems can be readily solved through the application of statistical technique, it is emphasized that, in order to arrive at correct conclusions, proper classification of data must be made. Such classification depends upon the skill and technical
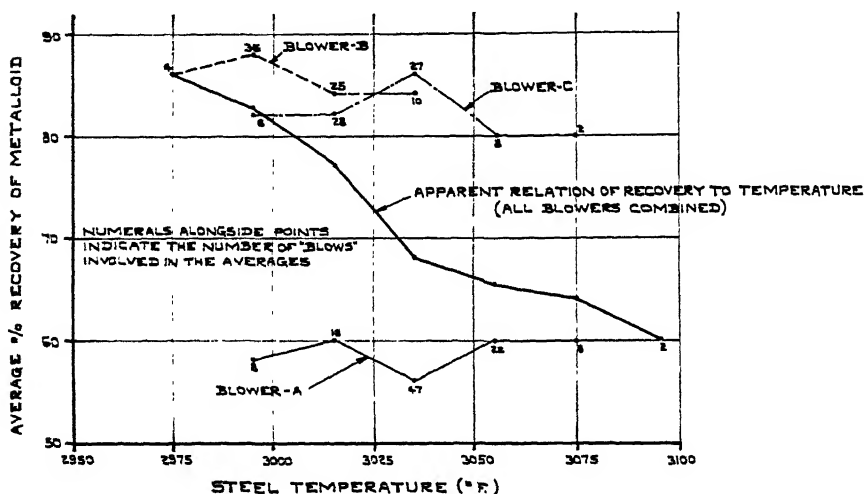
FIG. 2.—RELATION OF RECOVERY OF A METALLOID IN BESSEMER STEEL TO STEEL TEMPERATURE. AN APPARENT RELATIONSHIP DUE TO FAILURE TO WORK WITH RATIONAL SUBGROUPS OF DATA.

Effect of Blower on Temperature and Recovery

Blower	A	B	C
Number of observations	105	75	71
Average temperature, deg. F	3,037	3,006	3,027
Average percentage of recovery	58	86	83

knowledge of the analyst, and upon his practical experience with the process under study. For this reason, best results can be obtained when one familiar with a process acquires the technique of handling data statistically, rather than when one totally unfamiliar with the process, but highly specialized in the technique, analyzes the data. A sound knowledge of methods of application is necessary. Many examples

could be given of erroneous conclusions obtained from failure to properly subdivide data, but it is believed that the example of Fig. 2, showing the apparent effect of steel temperature on recovery of a metalloid used in making Bessemer steel, will illustrate the point. Note that recovery and temperature are not at all related, when the steel produced by blower is considered. The apparent relation arose because of the association of high temperature and low recovery with one blower. The recovery with blower A was found to have resulted from another cause entirely.

FREQUENCY CURVES

The frequency curve is perhaps the simplest of the statistical devices available. Daeves[3] gives a detailed exposition of its utility. In the following, some of the more important uses of these curves are pointed out. Attention is also directed to some shortcomings of this device, and to the need for some of the more complicated statistical devices—significance tests, control charts, correlation methods.

Some Important Uses of Frequency Curves

As undoubtedly appreciated from a consideration of the examples of Fig. 1, the frequency curve is a good method for presenting important information contained in repeated observations of a variable. The mode and total range of variability can be determined at a glance. The method of variation between extremes can also be observed, and any asymmetry or presence of secondary or double modes can be noted. A mistake easily made when interpreting the frequency curve should be avoided; i.e., attempting to determine the percentage of observations lying within any two limits from the polygonal method of plotting (used in Fig. 1).*

If a frequency curve has secondary or double modes, it is possible that "assignable" causes of variability (specific causes that should be detectable) are present, although not necessarily so. These may also result from irregularities due to insufficient observations or from the method of handling the data. If real secondary or double modes are present, proper subdivision of data should reveal their source and factors that contribute to abnormal variability identified. Examples of curves with real secondary or double modes have already been considered (Figs. 1c and 1d).

The frequency curve is also useful in detecting altered data, such as may result near limits of acceptable variability, or from a preference for whole numbers when observations are being recorded to the nearest half

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* If it is desired to obtain such a figure, the histogram method of plotting, exemplified in Fig. 3a, should be used; or better yet, the cumulative distribution should be plotted. With the histogram, the percentage of observations included between two limits is the relative area under the total block-type curve lying between them.

(Fig. 3a). (Observe the clustering of observations at whole numbers and near limits of acceptable variability.)

Frequency curves also have utility for comparing two conditions. When sufficient observations are available for plotting curves with relatively smooth contours, *important* differences between conditions can *usually* be detected. Comparisons utilizing frequencies, rather than averages, are desirable. When averages alone are compared, it is not known whether a few unrepresentative readings produce the difference.
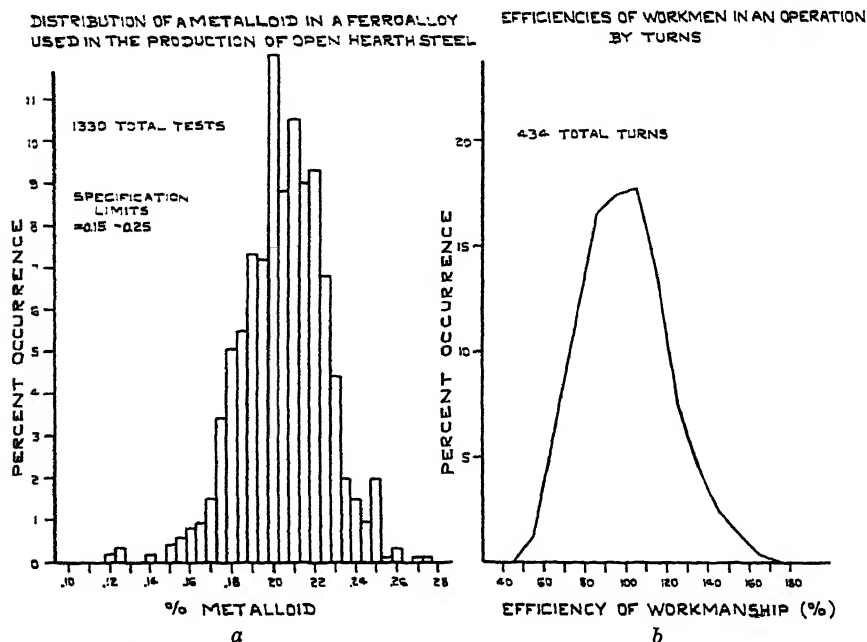
FIG. 3.—EXAMPLES OF FREQUENCY DISTRIBUTIONS IN INDUSTRY.
a.—Histogram type of curve showing altered data.
b.—Nonchance distribution having uniform appearance.

More reliance can be placed in the comparison if it can be seen that all measurements for the second condition have changed *proportionately* in relation to the first. Outstanding differences in *variability* for each condition can also be observed. The example of Fig. 4 illustrates the use of frequency curves in this connection.

The actual importance of variables of possible influence in the regulation of an observed result can be determined by utilizing frequency curves. If sufficient observations are available, frequencies of the condition under observation might be compared for different values of the variable of possible influence. Distributions of variables of possible influence might be divided in halves or thirds, for instance, and frequencies of the observed
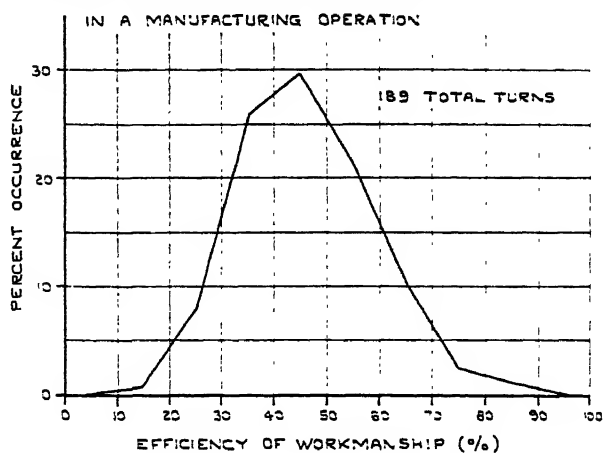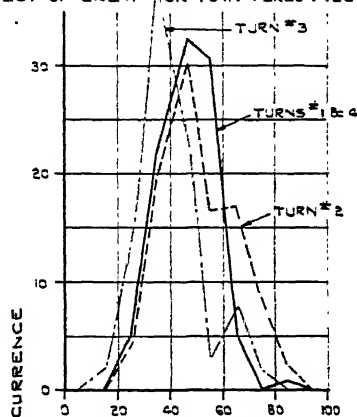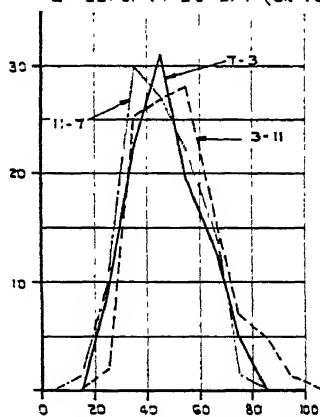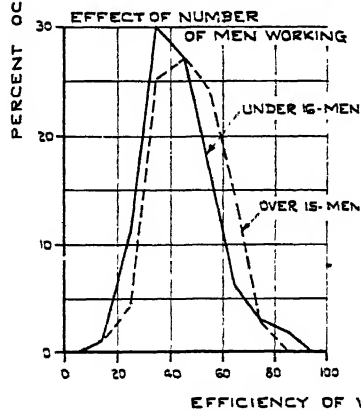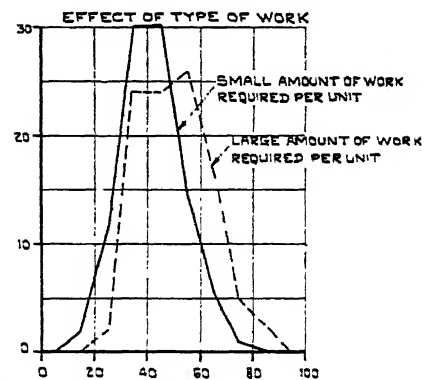
FIG. 4.—USE OF FREQUENCY CURVES TO DETERMINE IMPORTANCE OF VARIOUS FACTORS IN INFLUENCING AN OBSERVED RESULT.

condition compared.   The examples of Fig. 4 (an analysis conducted to determine which variables are important in the regulation of efficiency of workmanship in an operation) illustrate these points.   In this particular work, variable quality of material is furnished to the men, different numbers of men are used, and operations are continuous.   Distribution of shop efficiency was found as represented at the top of the figure. The effect of crew personnel, time of day (or turn), number of men working, and quality of material (or type of work) on efficiency is shown. When using curves in this connection, distributions of the variable under consideration for different values of ineffective factors will practically overlap; while similar curves for different values of effective factors will differ in dispersion or modal position.   Thus, it is seen that time of day is an ineffective factor (curves for the three shifts practically overlap). Crew 2 has the best efficiency; crew 3 the poorest.   Best efficiency apparently results when a large number of men are working, and when they are working on material requiring the greatest expenditure of effort (material of poorest quality).

Limitations of Frequency Curves—Need for Other Statistical Devices

The frequency curve has many serious limitations in the analysis of data.   First of all, if data are summarized only by means of the frequency curve, information relative to the existence of assignable (nonconstant acting) causes may be completely unrevealed, and good leads as to how to minimize excessive variability may be overlooked.   It is practically impossible to determine the existence of such factors from the appearance of frequency curves.   It will be recalled, from the examples of chance curves already discussed, that distributions arising from chance alone need not be symmetrical.   They may have a variety of shapes, depending on which law of chance is involved.*   Perhaps the simplest and most useful method of analysis for isolating assignable causes is Shewhart's control-chart method, to be discussed subsequently.   Although it would be difficult to suspect the presence of assignable causes from the frequency curve of Fig. 3b, the control-chart method indicates that part of the variability results from causes of this type, as may be seen in Fig. 7a. Note how similar the distribution of Fig. 3b appears to be to that of Fig. 1a, yet that of 1a results from chance alone, while 3b does not.

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* Distributions resulting from chance alone may vary in shape between the normal curve for billet sizes shown in Fig. 1a to the extreme J-type for defects in Fig. 1b.   They may be similar to Fig. 1a except for an asymmetrical tailing off toward either higher or lower values (second approximation curves).   They may resemble the J-curve of Fig. 1b, except that the mode may occur at 1, 2, etc., per cent defective, and tail off gradually toward the higher rejects.   Such curves may be characteristic of chance defects in processes in which rejects are substantial.   Many other types of chance curves exist.   It is beyond the scope of this paper to call attention to these in detail, but it is desired to emphasize their existence.

While frequency curves are superior to averages when comparing two conditions for a large number of observations, they are of no assistance for small-scale tests. With these, a special statistical device—the significance test—is essential for reliable comparisons. This test may also be desirable with large samples, when differences between conditions are not great, particularly when comparing *variabilities*. Through the application of these tests, decision as to whether observed differences result from chance or represent true differences between conditions is divorced from judgment alone. Various statistical characteristics of the data are calculated and compared to a criterion for action. Only if these exceed the criterion is the difference considered real, so that the risk that the observed difference is due to chance and yet considered real, is quite small, indeed. In the last analysis, these tests are the only rational basis for action when making comparisons, but, based on experience, simple comparison of frequency curves generally gives satisfactory results when working with a large number of observations.

For comparing many conditions simultaneously, where it would be necessary to compare numerous frequency curves at one time, better results can be obtained if various statistics characterizing the distribution are utilized, rather than the curves themselves. It is cumbersome to compare many conditions using only frequency curves, and quite difficult to draw correct conclusions. Desirable statistics to use are generally the *average*, and some measure of variability of individual values (such as the *range* or *standard deviation*).* When making such comparisons, the control-chart method should be utilized. Part or all of the observed differences in averages or standard deviations may be the result of chance. This device enables such differences to be distinguished from significant ones (through comparisons with statistical criteria, similar to those used with significance tests).

While frequency curves are useful for analyzing conditions to determine which variables are important in the regulation of a result desirable to control, better methods to utilize are those of *correlation* (discussed subsequently). Errors at times inherent when comparing frequencies can be avoided. For the example of Fig. 4, correlation studies indicated that actually efficiency is *poorest* with *large* numbers of men, not with *fewest*, as revealed by the frequency curves. Efficiency was found best

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* Other statistics of the distributions, such as skewness and flatness, may also be calculated, but these have not proved of such extensive utility as the average or standard deviation. Definitions and methods of calculating these values are given in the 1933 A.S.T.M. Manual on Presentation of Data.[3] The use of the range as a satisfactory statistic of a distribution is dependent on the number of observations (applicable only for 15 or less). The number of observations should always be considered when comparing statistics as the stability of these depends on the amount of data considered.

when large numbers of men were working, using the latter device only because number of men working, nature of the work, and efficiency are all interrelated.   A similar comparison made for men working on material of *like* quality would indicate the true conclusion; i.e., an increase in number of men decreases efficiency.

SIGNIFICANCE TESTS FOR COMPARING CONDITIONS

Desirability.—Perhaps everyone that has had to determine from experimental results which of two conditions is the better has hesitated at times to draw conclusions because of indecision as to the reality of differences observed in averages or variability.   Are the observed differences the result of chance and would it be reasonable to expect the reverse conclusion upon repetition of the test, or do they reflect actual differences between conditions or an improvement in a process?   This question is likely to arise when drawing conclusions from results of small-scale tests, but may also be encountered when analyzing large quantities of data, if differences between averages are relatively small, or if variabilities are being compared.   Through the use of statistical tests of significance, decision may be made on a mathematical basis (from certain statistical calculations involving the data for the conditions being compared), rather than merely from judgment based upon the existent difference.

The fact that the same difference between averages may or may not be *significant*, depending on the number of samples involved, and on the *dispersion* of individual values for each condition, accentuates the need for such a test.   Based upon the data on hand, an average of 12.0 for one condition and of 9.0 for the other may be indicative of a definite (significant) difference, if the individual observations have narrow dispersion; but may be insignificant for the same degree of testing, if they are widely dispersed.   In a like manner, the difference between the same averages might be significant with wider dispersion of individuals for more extensive testing (a greater number of observations).

Calculations involved in the application of these tests are well described by Fisher[4] and Tippett.[7]   Various statistical constants of the two sets of measurements are calculated and compared with a criterion for action.   If the criterion is exceeded, the difference is considered real; if not exceeded, it is considered the result of chance.   The criterion is selected so that if the action taken is always in agreement it may be expected that the decision will be wrong on the average a certain proportion of times, the level selected in a given case depending both upon what is logical and upon the importance of the decision.   Various levels of risking erroneous conclusions are used, but generally either that of being wrong one time in 20* or in 370* is selected.

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* Known as 2σ (twice standard deviation) and 3σ limits, respectively. See

It is desired to emphasize at this time that *statistical significance* should not be confused with *economic desirability.* Two conditions may be statistically different from each other, yet the difference may not be sufficiently great to make it economically desirable on a cost basis to favor one over the other.

Examples of Application.—The use of these tests in connection with small-scale experimentation is exemplified in Table 1, where two methods of sampling shipments of a raw material are compared, based on rather limited data. Actual differences in metalloid content as determined by the producer from that obtained by the consumer are shown for two

TABLE 1.—*Significance Tests for Comparing Two Conditions with Small Samples*

CHECK BETWEEN METALLOID CONTENT OF SHIPMENTS OF MATERIAL AS ANALYZED BY PRODUCER AND CONSUMER FOR TWO METHODS OF SAMPLING IN CONSUMER'S PLANT

Observed Differences

Check between Producer and·Consumer (Percentage of Metalloids)

"+" Differences—Consumer Highest

Sampling Method A			Sampling Method B	Difference between Methods A and B
+0.38	−0.74	− 0.70	−0.59	
+0.84	−0.59	+ 0.38	−0.47	
−2.05	+0.58	− 1.48	−0.71	
−0.63	+0.61	+ 0.36	+0.29	
−0.84	−0.54	− 0.82	+0.49	
−1.27	+0.39	− 2.12	+1.03	
−1.19	−0.35	+ 0.64	−1.48	
−0.82	+0.10	− 2.51	−0.14	
−0.62	+0.21		−0.97	
−0.55	−1.82			
Total number of samples......	28		9	
Average difference between producer and consumer.....	− 0.541		−0.283	0.258
Standard deviation of difference between producer and consumer.................	0.917		0.719	
Ratio of standard deviations (A to B).................			1.28	

Results of Significance Tests

2 σ level* for difference between averages = 0.667.

2 σ level* for ratio of standard deviations = 1.70.

Since the actual difference between averages (0.258) and ratio of standard deviations (1.28) is less than the limit values, the observed difference between sampling methods should be interpreted as being due to chance, and method A considered as good as method B.

* See Tippett[7] or Fisher[4] for method of calculating. The limits depend both on the dispersion of individual observations under each condition, and on the number of tests involved.

methods of sampling used by the consumer. Average differences and the standard deviation of the differences are also presented. Is the difference between sampling methods due to chance, or should sampling method B be considered superior? (Smallest *average* deviation from zero and smallest standard deviation.) Sampling this particular raw material by method B entails considerable additional expense, so that it is highly desirable to sample as few shipments as possible in this manner, unless definite improvement results. The table indicates that no significance should be attached to apparent differences between the two methods. Without the aid of this test, considerably more samples representing condition B would undoubtedly be desired, before concluding that observed differences were not real; and even so, error may have been made in the final judgment as to the merits of either method. As a result of this test, method B was quickly shown not to be an improvement over method A, and a prompt return to the less expensive method A was effected.

The significance test is frequently used in efforts to isolate factors causing trouble. Often considerable data are accumulated on a problem, but the (rational) subgrouping required may be so extensive that only a relatively few data are left for the investigation of the effects of certain other factors.

The following example will serve to illustrate this point. In the investigation of a difficulty experienced with a certain grade of steel, some 200 heats were available for study. Preliminary analysis of the data indicated that the size of ingot used and the method of reduction of the steel were closely associated with the particular quality in question. Classification of the data into rational groups according to ingot size and method of reduction was, therefore, required before the influence of other factors on the difficulty could be investigated. Such classification left only a few heats in each group. Need for significance tests while evaluating the effects of other factors will, therefore, be appreciated. By means of these tests the following additional factors were *definitely* found to directly affect the difficulty experienced: (1) state of oxidation, (2) amount of final additions made to the steel, (3) temperature of rolling.

CONTROL CHARTS

Utility and General Description

The control-chart method is useful for determining whether variability in a condition under observation should be expected as a result of chance or is caused by assignable factors. Limits* of chance variability are

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* As with significance tests, either 2σ or 3σ limits are generally used, the latter perhaps being generally preferable with the charts, since experience has demonstrated that these are a good basis for action on economic grounds. If action is taken

calculated from the data, and observations exceeding these are very likely to have been affected by an assignable cause. The method, thus, has great practical utility as providing a basis for *action;* a criterion for *cause hunting.* Definite reasons for most occurrences exceeding limits should be ascertainable.

Control charts are admirably suited to the solution of two general types of problems: (1) those involving a routine check on conditions, (2) those dealing with comparisons between numerous conditions simultaneously.

Charts are always set up for small subgroups of observations rather than for individuals.[6] In a given case, one of two fundamentally different types of charts should be constructed, depending on the type of data considered. One type is used for *rejects,* or observations not conforming to a given standard. The other is used when dealing with actual measurements of the object or factor under consideration. With the former, limits are needed only for the variation in number or *percentage of defectives* occurring in the subgroups; while in the latter limits are needed for fluctuations in the *magnitude of actual measurements* that are considered as due to chance. In the latter, limits for averages of the subgroups as well as for their variability* are required, if a complete check on the existence of assignable causes is to be made.

When a chart indicates that all variability of a certain characteristic of a process resulted from chance, and results are considered as too variable to be satisfactory, *fundamental* changes should be made in the process. These changes will alter the frequency with which all results are obtained. The chart shown in Fig. 5a, for sizes obtained in rolling

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when results exceed the 2σ limit, trouble or assignable causes are hunted for needlessly on the average of about once in 20; if action is based on 3σ limits, trouble is wrongly sought on the average of only once in some 370 cases. The limit chosen should depend upon the relative value of expending increased effort searching for trouble needlessly and that of overlooking an opportunity to locate an assignable cause when there is reason to believe that such a cause may have been operating. In the charts described herein, 3σ limits have been used for all problems except one—that for accidents (Fig. 5b). For accidents, it is of utmost importance to eliminate adverse conditions, so it was felt worth while to expend effort looking for trouble needlessly in an increased number of cases rather than to overlook any opportunity for locating causes of trouble.

* The latter should always be worked out in terms of *standard deviation,* unless groups are small (15 or fewer observations), when the *range* can satisfactorily be substituted for the latter. Because of the time saved when making calculations, use of the range is highly desirable where its use is permissible. Limits for *variability* are needed in charts of this type in order to detect the presence of assignable causes not detected by the *average.* For example, an abnormally *high* value due to one assignable cause might occur in the same subgroup of observations as an abnormally *low* value due to another cause. Such a condition might result in a normal average, but the variability would be large and the abnormality detected in this manner.

- BILLET SIZES ON HEATS OF STEEL WHILE ROLLING 8¼" BILLETS -
(SAME DATA AS SHOWN IN FIG. 1a)

EACH POINT= AVG OF 4 CONSECUTIVE HEATS
ONE BILLET CALIPERED PER HEAT
3 σ LIMITS SHOWN

EACH POINT= MAX - MIN DIA IN 4 CONSECUTIVE HEATS

GROUP OF FOUR CONSECUTIVE HEATS ROLLED
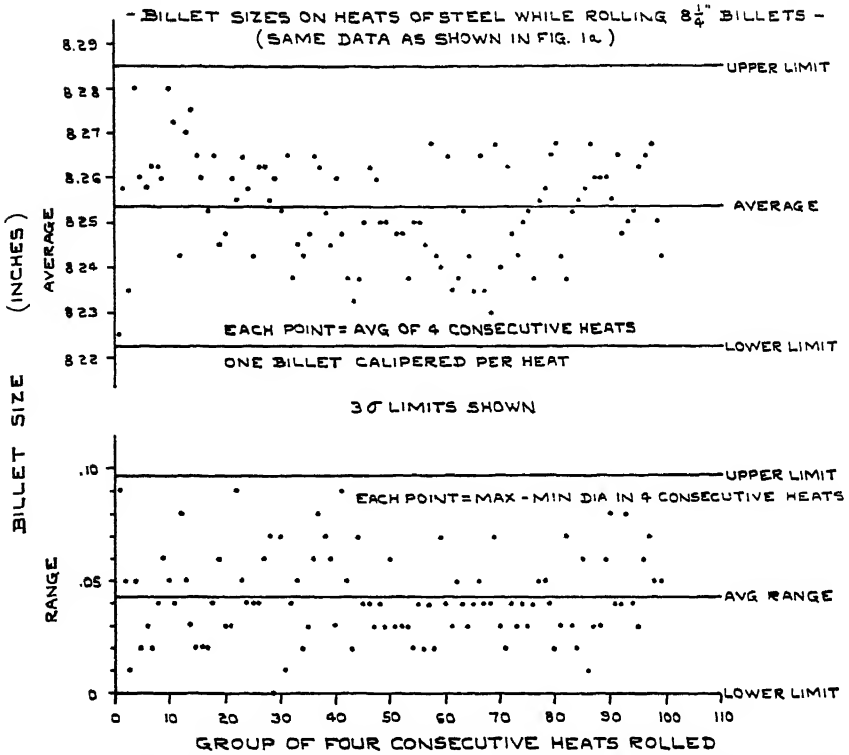
a.—Applicable when dealing with actual measurements of the characteristic in question.

- LOST TIME ACCIDENTS -

EACH POINT SHOWS THE NUMBER OF ACCIDENTS DURING 3,000,000 MAN-HOUR PERIODS
2 σ LIMITS SHOWN

SUCCESSIVE PERIOD OF 3,000,000 MAN HOURS
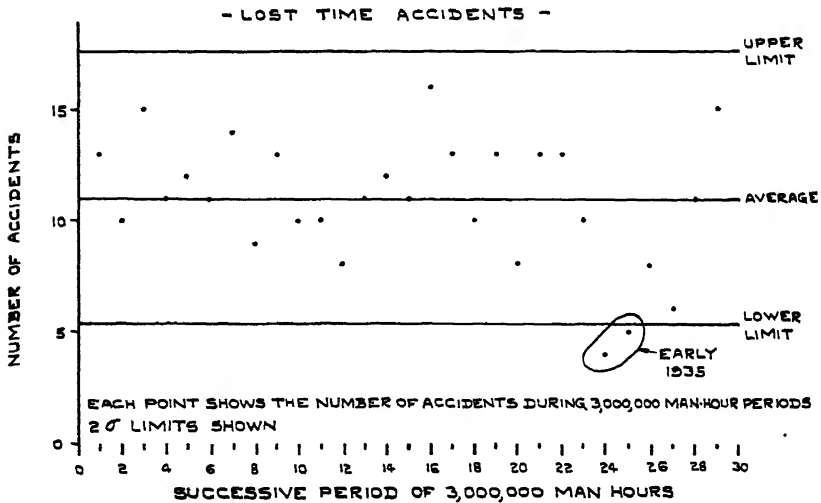
b.—Applicable when dealing with observations not conforming to a standard.

FIG. 5.—EXAMPLES OF USE OF CONTROL CHARTS IN INDUSTRY.   TWO FUNDAMENTALLY
DIFFERENT TYPES OF CHARTS USEFUL FOR ROUTINE CHECKING.

steel billets of a specified cross section (for which the frequency distribution was presented in Fig. 1A), is an example of variability resulting from chance alone. No value, either for average or range, exceeds the expected limits of variation. Even though the maximum and minimum sizes produced might be undesirable for further fabrication, it would be useless, in a given case, to attempt to isolate the specific cause of the trouble. Here the largest and smallest sizes result from unusual chance combinations of all factors causing variability, as discussed in connection with Fig. 1a. Fundamental changes, such as improved screwdown control or improved wearing quality of rolls, etc., might, on the other hand, be helpful in eliminating the extremes.

An example of a chart for number (or per cent) nonconforming to a standard, is given in Fig. 5b. Lost-time accidents might be considered in such a manner, if dealt with in terms of *number* of accidents occurring in 100,000 or 1,000,000 (or any number) of man-hours of exposure (since in any instant a lost-time accident either does or does not occur, and an instant with an accident might be considered to "nonconform" to the standard of no accidents). Fig. 5b is a chart for accidents for successive periods of 3,000,000 man-hours. Because of the relatively few man-hours in which accidents occur, it was necessary to select groups of man-hours as large as this, in order to detect an improved condition, if such existed. The lower limit of *chance* variation in accidents to be expected even in a 1,000,000 man-hour period is less than 0, so that even if improvement actually existed, charts based on relatively small batches of man-hours would not conveniently indicate it. On Fig. 5b 2σ limits are used, for, in problems such as this it is desirable to look for the cause of the trouble needlessly at times rather than not to investigate when it is quite probable that some adverse condition that could be isolated had been present. Factors affecting lost-time accidents should be detected as a result of the continued use of a chart such as this, even though for the data shown the cause of the definite improvement in 1935 could not be ascertained. A chart of this type should prove of exceptional value when endeavoring to determine whether campaigns or drives for safety accomplish desired results.

Practical Examples of the Application of the Control Chart

Many interesting examples of the application of the control-chart method are shown in Figs. 6, 7 and 8:

Chart for Impurity Present in Raw Material (Fig. 6a).—This chart shows the daily average content of an impurity present in a raw material used in the production of steel.* Because of the variation in the *number*

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* If it is desired to make a *complete* check on the existence of assignable causes, charts for *variability* as well as averages, should be carried, both on this chart and on the others presented in Figs. 6 and 7. Such charts were constructed, but are omitted here because no additional irregularities of prime importance were detected.

of tests taken daily, limit lines are not shown on the chart. *Abnormal* days (days with assignable causes of variation in the impurity), are shown as *x*.* Note the period of high impurity occurring during June. Here,

a.—Impurity present in a raw material.

b.—Yield of production from a rolling mill.

c. Rate of production in a process (data same as those of Fig. 1*c*).
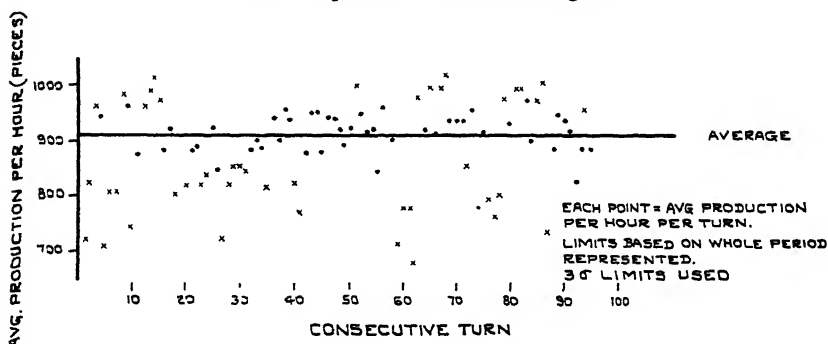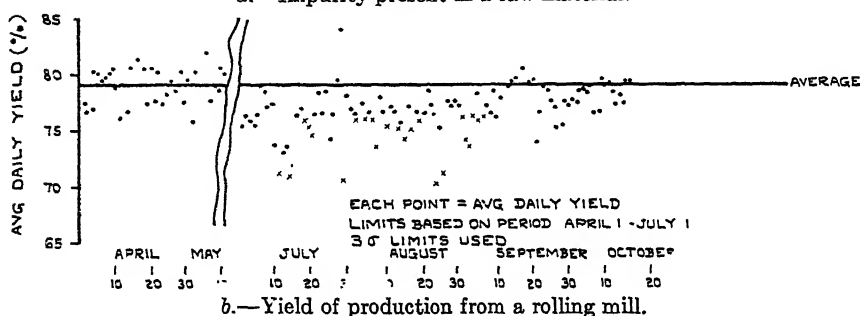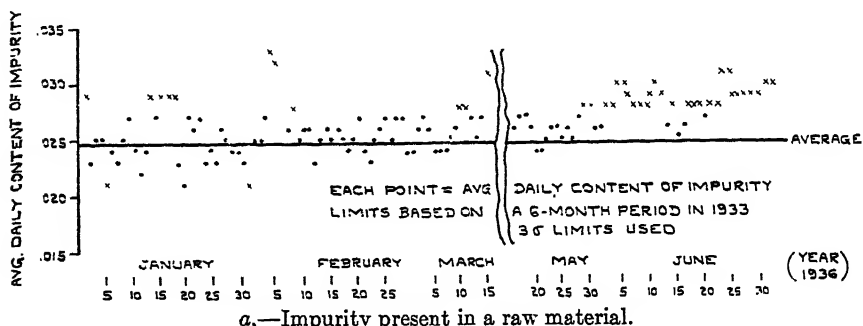
FIG. 6.—EXAMPLES OF USEFULNESS OF CONTROL CHARTS IN INDUSTRY. ROUTINE CHARTS INDICATING ENTRANCE OF ASSIGNABLE CAUSES.

it is seen, an assignable cause has entered the system and remained for a considerable period of time. The chart detected its presence imme-

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*Limits of chance variability vary with *sample size*, or *number of observations* in the batch under consideration, according to well defined statistical laws, becoming *narrower* for *averages* with increasing size of sample.[8] Limit lines are not shown on the chart in question, due to the confusion incident to the appearance of widely fluctuating limit lines.

diately. After extensive investigation the specific reason for high impurity was found, and upon its elimination, conditions returned to normal. Table 2 indicates how the impurity content of individual tests increases during the abnormal period under discussion (June) over a normal period (January).

Chart for Yields of Product from a Rolling Mill (Fig. 6b).—This chart shows the average daily percentage of product of a certain type of steel obtained from a rolling mill. Days on which abnormally reduced good product was obtained are again marked x. This chart was established when it was the standard practice to produce heats in a certain manner. In an effort to secure a change in physical properties, the method of

TABLE 2.—*Meaning of Lack of Control in Terms of Frequencies*
COMPARISON OF IMPURITY IN A RAW MATERIAL DURING HIGH AND NORMAL PERIODS

June (High Period)		January (Normal Period)
0.027	Mode	0.022
0.0286	Average	0.0249
37.14	Percentage of tests 0.030 or over	15.80
16.17	Percentage of tests 0.033 or over	7.53
8.57	Percentage of tests 0.035 or over	3.84
5.10	Percentage of tests 0.037 or over	1.48
2.22	Percentage of tests 0.040 or over	0.30
10	Number of tests 0.042 or over	0
763	Total number of tests	677

producing the steel was changed in early July. Note how quickly the chart detected the detrimental effect on satisfactory product; i.e., the many abnormally low points for latter July, August, and early September. Upon return to the former method of production, normal conditions were again obtained.

Chart for Rate of Production in a Certain Process (Fig. 6c).—This chart shows the variation in average production of a certain commodity by turns. Turns found to be abnormal, owing to the variation in time spent on the particular commodity from turn to turn, are again marked with x. The lack of controlled conditions is apparent. In 28 turns (29.9 per cent of observed turns involved), abnormally *low* production resulted. Causes of this low production were found to be: (1) starting on a "run," (2) sticking in mechanical units, and (3) defective raw material. Many of the turns with *high* production were found to be associated with a particular crew, which subsequent investigation revealed consistently produced about 15 per cent more than other crews. Data represented in this chart are the same as shown in Fig. 1c for individual hours worked. Secondary modes observed on that curve resulted from the points shown to be abnormal on this chart.

Chart for Efficiency of Workmanship in an Operation (Fig. 7a).—
Charts such as this are useful in maintaining a routine check on efficiency
of workmanship (based upon the percentage ratio of actual working time
to that allowed for the job). This example, incidentally, illustrates the
relationship between statistics and time study. After standards have
been set up by time study, statistical methods are valuable in inter-
preting daily deviations from them. Statistical methods should not be
used for determining how much work can be done from past production
records (unless the operation is efficient), but as soon as standards are

a.—Efficiency of workmanship in an operation (data same as those of Fig. 3*b*).

b. Surface quality of machined product.
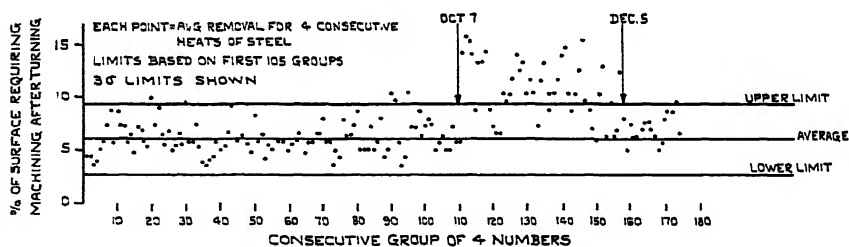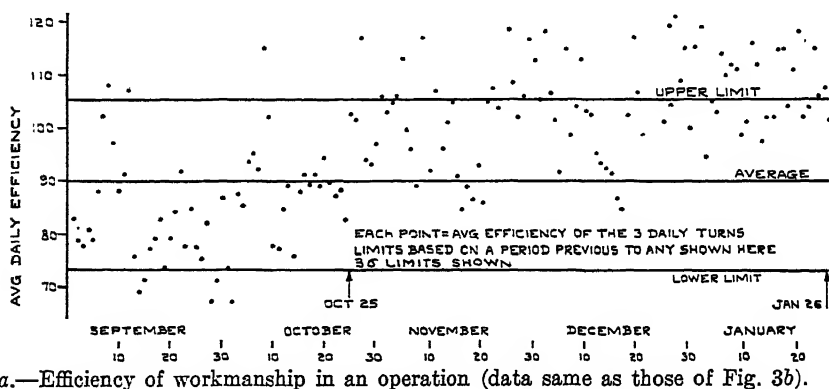
FIG. 7.—EXAMPLES OF USEFULNESS OF CONTROL CHARTS IN INDUSTRY. ROUTINE
CHARTS INDICATING ENTRANCE OF ASSIGNABLE CAUSES.

set by time study, statistical methods are important in following
up results.

Notice the general rise in efficiency starting abruptly on Oct. 25.
While many days exceed the upper limit, it appears likely that there has
been a *shift* in average level of efficiency starting on that date. All points
after Oct. 25 are normal with respect to limits based on new averages cal-
culated from Oct. 25 to Jan. 26. Comparing averages before and after
Oct. 25, the significance test indicated that a definite and *significant* shift
in averages took place, and that the whole system of observations after
Oct. 25, considered as a unit, is abnormal with respect to the older

condition.* Definite explanations were available for the sudden rise in efficiency.

Chart for Surface Quality of a Machined Product (Fig. 7b).—Charts such as this have been found useful in maintaining a daily check on surface quality of a product that is turned on a huge lathe followed by removal of defects. Because of the rational subgrouping required, only grades of steel having the same inherent surface characteristics can be included on a given chart, so that more than one chart of such a nature may be required for a complete check on conditions. Fig. 7b shows the variation in additional machining (chipping or torch cutting) required after turning. By following this daily, important changes in steel quality are readily detectable, and steps can be taken immediately to eliminate factors producing inferior quality.

In the example of Fig. 7b, quality was adversely affected on Oct. 7 and remained so until Dec. 5. During the normal period (Feb. 16 to Aug. 25), 6 per cent of the surface had to be machined after turning, and during the inferior period, 11.6 per cent (Oct. 7 to Dec. 5). This increase amounted to nearly 4000 man-hours. After an extended investigation, it was found that a general shift in diameters of the product to be turned was causing the trouble. In the turning operation, a product of specified diameter is produced. Soon after the adverse period started, an investigation disclosed that the *additional* machining required was very sensitive to the amount of metal removed in the original turning, additional machining *increasing* rapidly with the lesser amount of original metal removed. Beginning on Oct. 7, it was found that owing to a change in method of rolling, rounds of a somewhat smaller diameter were being produced, which required higher machining after turning because less metal was being removed in turning. Upon elimination of the factors responsible for this shift, surface quality returned to normal.

Chart for Life of Rolls Purchased from Different Manufacturers (Fig. 8). All charts discussed so far are applicable to *routine checks* on conditions of importance to the plant metallurgist, industrial engineer, or various operating superintendents. A type of chart found useful when com-

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* This point should be borne in mind when interpreting any control chart. *Groups of points near* limit lines may all be within chance limits of variation, yet under certain circumstances should be considered fully as abnormal as one point lying outside the limits. The criterion should be: Are the points considered *together* outside the limit of chance variation for a sample of size equal to their combined total? The larger the number of observations involved, the smaller the deviation from normal needed to consider a condition as being abnormal. For the case on hand, the period Oct. 25 to Jan. 26 had 294 turns; and *limits* for the deviation of the average of *this whole period* from that of the past are only 10 per cent as wide as for those for daily points. It can be noted from observation of the figure that the new average would be more than 10 per cent greater than the old average, and thus the whole recent period is abnormal with respect to the older one.

paring manufacturers' products, and which could be made the basis for selection in future buying, is shown in Fig. 8. This chart compares the life of rolling-mill rolls obtained from four different makers. Both average life and *variability* of life from roll to roll are considered. While no significance should be attached to differences between averages, manufacturer C has the most variable or *inconsistent* product. It should be concluded, therefore, that the products of A, B or D should be considered equally desirable, but that of C inferior, because of lack of *dependability* (excessive variability). The cost of product of A, B or D will then become the influencing factor in choice of future purchases.
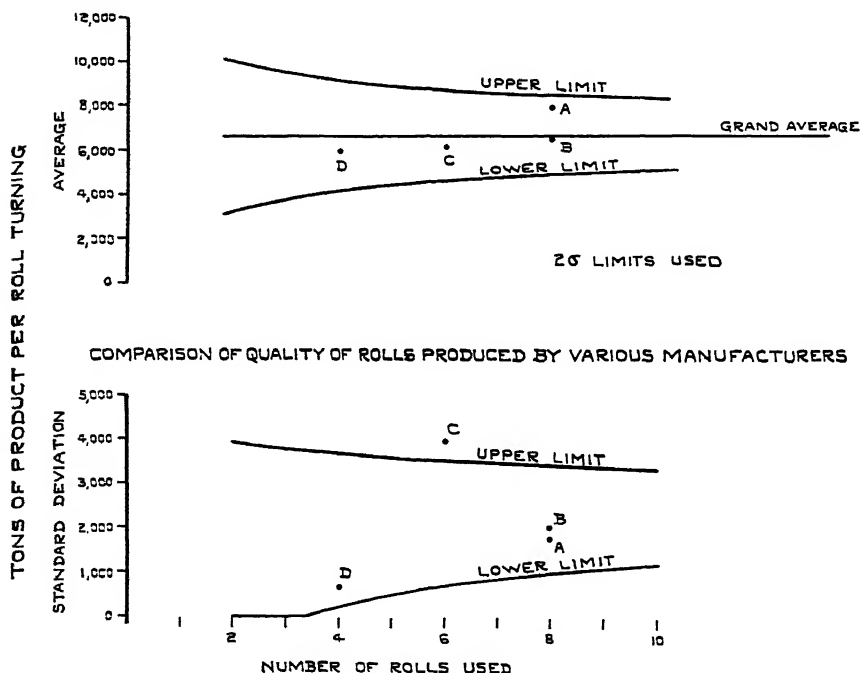
FIG. 8.—EXAMPLES OF USEFULNESS OF CONTROL CHARTS. USE OF CHART TO COMPARE NUMEROUS CONDITIONS SIMULTANEOUSLY.

The control-chart method will not function to good advantage with all types of data collected in industrial plants. When dealing with composite figures depending more on size of product made, number of men working, tonnage produced, etc., than on operating conditions, abnormalities revealed by the chart will be found to be due to good or adverse combinations of these factors rather than to anything representative of good or bad operating conditions. Control charts are of no value on such data. Many cost-rate figures (cost per ton) have been found in this category, unless indices of conversion can be established and used.

CORRELATION

Nature of Relationships between Variables under Operating Conditions. Many problems important to the analyst of steel-plant data deal with the determination of *relationships* between variables. Just as, when trying to produce a constant result in industry, identical values are not obtained, so also variability in relationship is found between factors. Instead of being able to represent the relationship between two factors with a *line, a band* (or area) must be used. For a given value of variable *A*, variable *B* will vary from *x* to *y*, which changes progressively as *A* increases or decreases. The range of variation of *B*, knowing *A* will be smaller than that within which *B* could be predicted, *A* being unknown.

A control-chart study may indicate that all variability present is to be expected as a result of chance, yet the variable in question may be found related or *correlated* quite well with several other factors. If these relations are *cause* and *effect*, factors found associated with and influencing the variable in question are themselves acting in a chance way, which will result in chance fluctuation for the variable. If the range of variability of such factors can be minimized through fundamental changes in the process, a definite decrease in the range of variation of the variable under consideration would be effected. Correlation studies, then, may prove valuable in suggesting various fundamental changes desirable to secure less extreme variability in a process, supplementing the control-chart study.

The relation between amount of work to be done per unit in an operation and hours required to do it, typical of a *good* relation between variables as encountered in industry, is portrayed in Fig. 9a. It is plain that these factors are related in some way, yet there is considerable variation in the hours required for a *given* amount of work to be done, or vice versa. Modern statistical methods offer a scientific method for attacking problems of this type. Through their use such relationships can be interpreted intelligently. Methods of dealing with such problems are known as those of "correlation."

Through the use of correlation methods, it is possible to obtain a statistic to show *how closely* two variables are related, known technically as the *correlation coefficient*. With the aid of this coefficient, it is possible to determine whether the relation at hand is definite (and reproducible upon the collection of further data) or due to chance (and not reproducible). Further, this coefficient is useful in predicting the range within which one variable can be expected to vary, given the value of the related variable.

Statistical Reduction of Data for Determining Relationship.—It is characteristic of statistical relationships that variation in the *average*
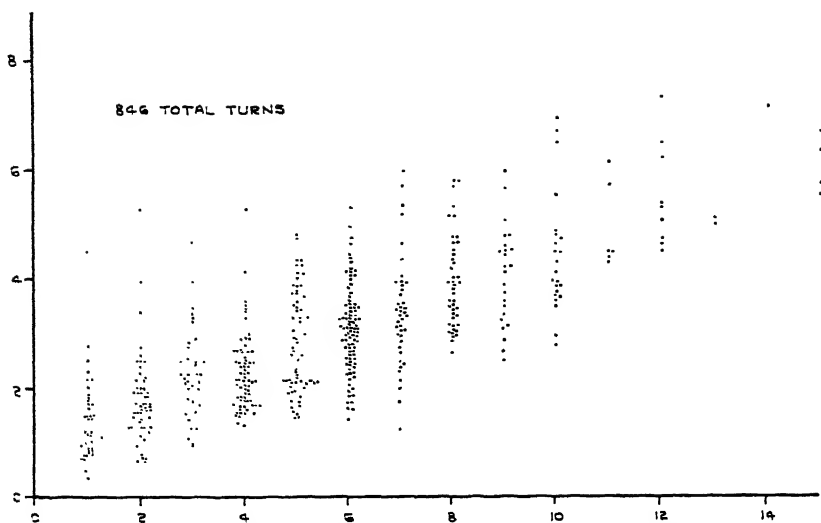
a.—Stereotyped "buck-shot diagram" or "scatter plot."
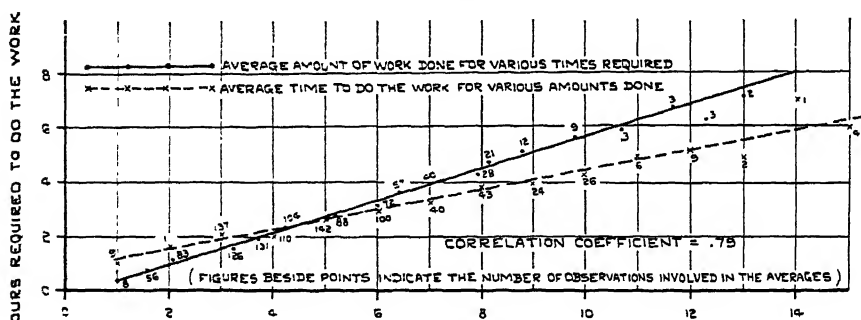
b.—Partial statistical reduction—correlation diagram.
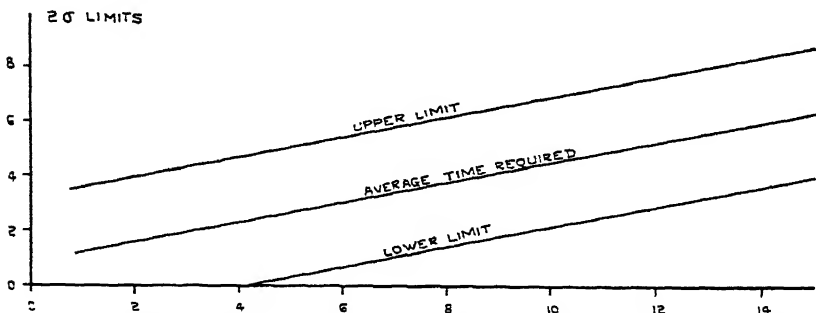
c.—Complete reduction—the band.

Fig. 9.—Typical of good relationship between variables found in industry. Relation between amount of work to be done and time required to do it.

value of *one variable* (hours required) as the *second* variable (work to be done) increases, *does not coincide* with variation in the *average* of the *second* as the *first* variable changes. When these two sets of averages are plotted for the data of Fig. 9a, Fig. 9b is obtained. The correlation coefficient can be calculated graphically from the lines for the two sets of averages. Other things being equal, as the angle included between such pairs of lines decreases, the association between the variables involved *increases*, and the absolute value of the correlation coefficient increases.*

With the aid of the correlation coefficient, limits can be set up about lines for either set of averages, so as to include various proportions of observed values, similar to limit lines on control charts. The relationship is then portrayed by a *band*, within which individual observations may reasonably be expected to occur. Such a band, set up about the average time required to do the work per unit for varying amounts of work to be done, is presented in Fig. 9c for the data of Fig. 9a. Fig. 9c is thus the statistical reduction of the buckshot diagram of Fig. 9a.

Examples of Utility of Correlation Methods.—The correlation coefficient may find useful application in comparing associations between variables before and after fundamental changes have been made in a process. An interesting instance of this, encountered in time-study work, is that involved in the relation between work to be done and time required to do it, before and after an incentive rate system was effective. If the incentive is operative as desired, various irregularities causing inefficiency should be eliminated, and variation in hours needed to complete the job should decrease for a constant amount of work to be done. Conditions before incentive were as represented in Fig. 9, where a coefficient of 0.79 was obtained. After incentive, the coefficient was 0.91. Variability in the time needed to complete the work for a given amount of work to be done, therefore, decreased some 38 per cent.†

The incentive system, therefore, had effected more uniform operation.

Many times, direct correlations between variables lead to false relationships, due to the association of each variable involved with a third. Mere plotting of the "buckshot" type of diagram (Fig. 9a) affords no method to develop the *true* relationship in such cases, except by plotting only those values of the variables between which the relationship is desired, when the third variable is constant. Such a procedure requires discarding of the great majority of observations and requires the use of many more data than are necessary for drawing conclusions. Through

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* The coefficient may vary between ±1, zero indicating no relation, and either +1 or −1 perfect relation; a positive value indicating that as one variable increases the other increases also, while a negative sign denotes decrease in one with increase in the other.[7]

† See Tippett[7] for method of interpreting increases in the correlation coefficient in terms of the decreased variability of one variable for a given value of the related variable.

the use of the correlation coefficient, however, *all* data can be used, and still the true conclusion developed.   If working with a moderate number of data, use of the correlation coefficient might be an absolute necessity, owing to the small number of data remaining after omitting that in which the third variable differs.

An interesting example of this use of the correlation coefficient is worked out in Table 3, showing the relationship between efficiency of workmanship in an operation and number of men working; one that was investigated by means of frequency curves in Fig. 4.   The direct correlation between efficiency and number of men working indicates that efficiency increases with increased numbers of men.   The same conclusion was attained when frequency curves were compared.

Table 3 also shows the relations between these variables with a third, i.e., amount of work to be done per unit.   Both the number of men and

TABLE 3.—*Use of Partial Correlation Coefficients to Avoid Error When Determining Statistical Relationships*

EFFECT OF NUMBER OF MEN WORKING ON EFFICIENCY OF WORKMANSHIP IN AN OPERATION

Interrelations between number men working, type of work done and efficiency
Correlation efficiency—number men working...................... +0.384
Correlation efficiency—amount of work done per unit............... +0.638
Correlation amount of work per unit—number men working.......... +0.893
Partial correlation between efficiency and men, with a constant amount of work done per unit... −0.536

the efficiency are *greater* with *increased* amount of work per unit.   Could not the greater efficiency with increasing number of men have resulted from the increase of each as the amount of work increased?   If the amount of work per unit were held constant, what would be the relationship between efficiency and number of men?   These questions can be answered with the aid of a partial coefficient, calculated from the correlation coefficients representing the three interrelationships.   With this device, it is possible to obtain the relationship between efficiency and number of men, holding the amount of work constant.   Such a value is presented in Table 3.   The negative coefficient indicates that added men mean *decreased* efficiency, exactly the opposite conclusion to that drawn from the direct correlation.   The apparent increase in efficiency with additional men, considering all data, was the result of the logical increase of men when more work was needed per unit, and of efficiency with this same variable.

Through the use of partial coefficients not only one but as many variables as desired may be held constant, so the actual relation between any two may be determined readily.[4,7]

The correlation coefficient is valuable for determining whether or not a relationship exists between two variables from the results of a very few

tests. For example, there should be no doubt of the association between the manganese content of blast-furnace flush slags and sulphur in the succeeding cast from the 14 paired observations of Table 4.

TABLE 4.—*Use of Correlation Coefficient for Determining Relationships from Small Samples*

VARIATION IN SULPHUR IN BLAST-FURNACE IRON WITH MANGANESE IN THE PRECEDING FLUSH SLAG

Observed Results

MANGANESE IN FLUSH	SULPHUR IN CAST	MANGANESE IN FLUSH	SULPHUR IN CAST
0.49	0.016	1.97	0.057
0.85	0.019	0.44	0.015
0.70	0.024	1.01	0.020
0.95	0.028	0.31	0.013
0.32	0.012	0.83	0.012
0.35	0.009	0.56	0.019
1.05	0.031	1.89	0.054

r = correlation coefficient = 0.95

The 3σ level for statistical significance of the correlation coefficient from 14 paired observations = 0.72. This is, therefore, indicative of a definite relationship, since coefficients of 0.72 or over could be obtained with no actual relationships between the variates on the average of only once in 370 cases.
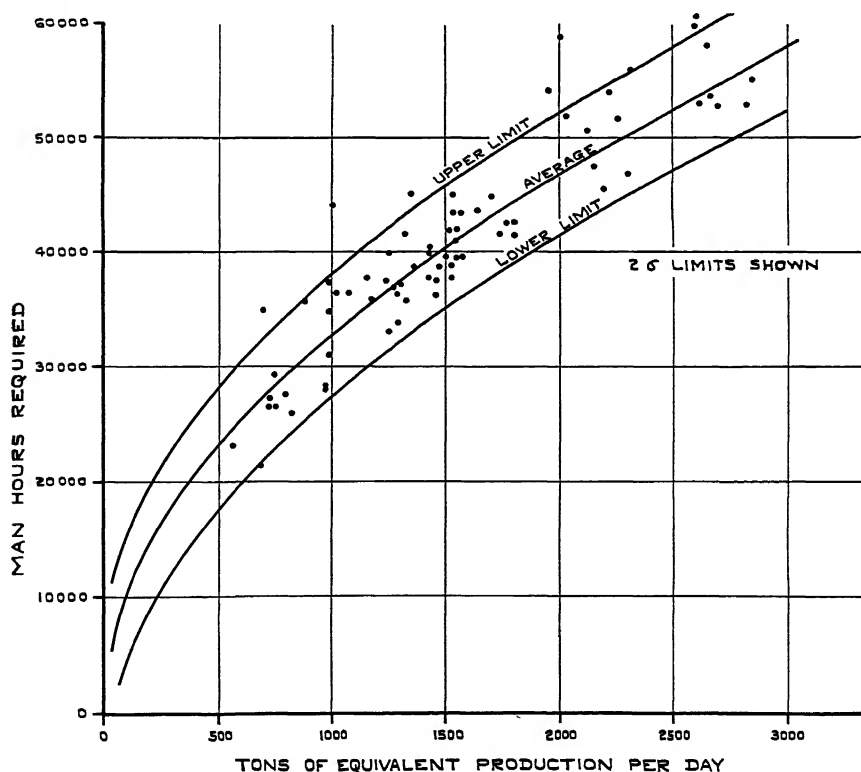
FIG. 10.—CHART FOR CONTROLLING MAN-HOURS RELATIVE TO PRODUCTION.

The correlation coefficient is meaningless if applied to curvilinear relationships between variables. Other methods are required, which will not be discussed herein, but an interesting example of curved relationship, of interest to operating men, is presented in Fig. 10. This chart shows the limits within which man-hours involved in production should be expected to vary for various semi-monthly tonnages produced. Such a chart serves to aid in maintaining the proper relationship between man-hours and tonnage, particularly during periods of expanding or diminishing business. Of the abnormally high points, the two farthest removed from the upper limit (at 1000 and 2000 tons production) were in a period of rapidly expanding business. The chart indicates that hiring of men was probably too rapid for the ability to properly absorb them in production, an unsatisfactory condition for economical operation. Other periods having excessive man-hours were found associated with: (1) rapid decreases in production, (2) increased labor involved in the stocking and shipping of a product after a long period of good operation, when heavy stocks accumulate, (3) periods of vacations with pay (vacation man-hours being charged to such production as there was during the period involved).

Data Not Capable of Statistical Analysis

Before concluding, it is only fair to point out that many data *as now accumulated* in the industrial plant are practically valueless from the statistical viewpoint; they cannot be interpreted satisfactorily or used for purposes of production or quality control. This subject alone could very easily be made the topic for a paper. A few examples of such data are given:

1. *When trying to control a given characteristic of a process, the use of composite figures as a measure of the particular characteristic involved that depend mainly on the type of orders executed, rather than on operating conditions.* Many cost rates fall into this category at present, where the cost per unit at the end of the month depends more upon factors such as tonnage made, hours worked, size and class of material, etc., than on operating conditions. If it is actually hoped to *control costs*, cost-rate figures that readily lend themselves to the formation of good relationships with *operating* variables must be made available.

2. *Reporting of material in wrong units.* This is particularly likely to happen when reporting rejects. The statistical unit for rejects is the relative *number* rejected to the *number* tested, not *pounds* rejected to *pounds* tested if materials having different unit weights are tested and results reported without size distinction.

3. *Use of averages representing chemical or physical characteristics of raw materials used in a process, when detailed reports as to the variability from batch to batch is desirable.* Averages over a considerable time period

mean nothing, of course, in the control of operations if the *variability* of a material obtained in batches is causing the trouble.

4. *Data on the variability of the characteristics of a raw material, which cannot be correlated with results of a process using this raw material to produce another material.* Correlation methods are not applicable here, as one must compare sustained periods of high or low values of the characteristic in question on operating results. This is a dangerous procedure, because of other possible changes that may have taken place in periods compared.

5. *Failure to identify conditions pertinent to each observed value of the result in question.* This is obviously bad, for, owing to lack of proper data, it makes rational subgrouping impossible.

If routine industrial data are to be properly interpreted, efforts should be made to record them with statistical principles in mind. It must be remembered that all that statistical analysis can do is to reveal the story that has been recorded with the data. The value of plant records (for statistical analysis) could be greatly increased undoubtedly if a statistically minded engineer were consulted in the matter of collection of data.

SUMMARY

The application of statistical methods to industry is still in its infancy, but because of the great utility of the technique, use of these methods is being extended rapidly. Many methods are now available for analyzing plant data, which should greatly increase the value of any analysis made. This is true not only for data intended for the plant metallurgist, but also for data dealing with time study, production, safety, purchasing, and scheduling problems.

While many examples of the application of these methods have been discussed in the present paper, many devices of use have not been mentioned at all, and only the "surface has been scratched" showing the various types of problems that can be worked out. Problems similar to those discussed herein in the isolation of factors producing abnormal variability may readily be solved in such diverse fields in steel plants as blast furnaces, coke plants, threading floors, rolling mills, galvanizing, etc. Factors affecting uniformity in quality of product made, or of influence on cost, etc., may be studied. This paper has been written only to arouse interest in the methods, by presenting several examples of their useful application.

Attention has been called to the existence of certain data in industrial plants that cannot satisfactorily be analyzed by statistical methods. This is true not only of data obtained as a matter of routine but also of that obtained in many special investigations. Production rates that are strongly affected by tonnage made, size of product, etc., rather than by

operating conditions, can hardly be expected to reveal much in the way of production control in a statistical analysis. Many times in special tests the wrong type of data are obtained; either they are not representative or conditions under which they were taken are ill defined. Too often, conclusions desired are misconstrued in the planning of tests and statistical principles are ignored. For broader use of the methods available, statistical principles should be consulted during *planning* and *not after results are obtained*.

ACKNOWLEDGMENTS

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DISCUSSION

(C. H. Herty, Jr. presiding)

J. JOHNSTON,* Kearny, N. J.—I wish to congratulate the author for a fine demonstration of how statistical methods may be used profitably to interpret data observed in the operation of a steel mill. Many are now using these methods, and I am confident that, as their usefulness becomes more widely recognized, they will be used more and more. They enable the mill to be used in effect as a laboratory in the many cases in

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* Director of Research, U. S. Steel Corporation.

which it is at present quite impracticable in experiments on a laboratory scale to take account of all of the factors that may bring about variation in the process or the product.

H. F. Dodge,* New York, N. Y. (written discussion).—Mr. Hand is to be congratulated on his colorful presentation of how statistical methods may be put to work in an industrial plant. The industrial engineer, like any other engineer, is constantly faced with the problem of interpreting data. But his data are commonly of a very significant variety in that they are associated with repeated series of like events occurring again and again under generally similar conditions. To this kind of data, statistical methods are peculiarly applicable. This paper, with illustrations drawn from all corners of an industrial plant, demonstrates an exceedingly interesting point; namely, that it matters little whether the data at hand relate to control of quality or to personnel problems, such as efficiency of production or lost-time accidents, the simpler methods of statistics apply equally well and the quantitative criteria which they provide are equally usable as guides for management action.

Often there is reluctance to employ statistical methods in the every-day operations of a plant, because they appear to be highly mathematical and require a special kind of skill and training. Mr. Hand's illustrations would tend to allay such a feeling, for admittedly he uses only the simpler statistical tools, those requiring very little mathematics.

Were we to ask what the methods really contribute to the solution of quality and other problems, the answer might fairly be associated with two words, economy and assurance. The methods place the spotlight of attention on that ever-present and important characteristic of things we measure, their variability from unit to unit and from time to time. When are observed variations due to assignable causes that may be tracked down and prevented from introducing spasmodic shrinkage losses, and when should observed variations be left to chance and not bothered with? The author shows how these and other questions have been answered to his satisfaction by employing the criteria embodied in the quality control chart and in tests for "significant differences."

Two features of the paper seem to stand out: (1) the importance of careful planning for the collection of data and (2) the advantage of presenting information graphically. Misuse of statistical methods often results from averaging large quantities of data with the thought that if enough numbers are thrown together one may find the underlying character of the variation through an "averaging out" process. The necessity for doing just the opposite, for tallying and keeping data in separate cubbyholes by rational subgroups is brought out well in Fig. 2 of the paper. Following the latter practice commonly provides the key to better data and to the discovery of the sources of trouble that would otherwise elude the harassed foreman. As to graphical methods, both the man in the shop and the executive can grasp a situation at a glance if shown variations or trends in picture form, whereas words may be just words. One way of getting started in exploring the possibilities of statistical techniques is to draw simple charts showing the results obtained from day to day, from month to month or from one group of workmen to another. The next step follows easily—the addition of limits of variation around the general average value, limits such as are provided by the control chart. How these may be handled is shown admirably in Figs. 5, 6, 7 and 8, and how such limits have been employed as a basis for action is well illustrated in the text.

This paper, with its variety of excellent illustrations, merits a careful reading by those who are interested in means for obtaining greater efficiency and economy in a manufacturing plant.

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* Member Technical Staff, Bell Telephone Laboratories.

C. H. HERTY, JR.,* Bethlehem, Pa.—I think that we can say one thing about statistical methods, particularly the ones that have been brought out today, and that is that every operating man and every metallurgist does this same thing mentally as he goes along, as his operations proceed and as he collects data for himself. He makes a mental statistical analysis because of the difficulty that he has with so many other things to think about. He forgets the trends that are taking place, and it is only by keeping them right along in black and white, as these particular methods are able to do, if you follow them up, that you are really able to take advantage of statistical methods.

I might mention one point in connection with Mr. Dodge's remarks. W. J. Reagan some three years ago, I believe, used one of the methods that Mr. Norris pointed out,[10] that of plotting the FeO against certain other variables with a constantly diminishing FeO, and that particular method immediately showed up the main variables, which accounted for the change in FeO in the slag from time to time.[11] It was a very clear-cut picture, and the point that Mr. Dodge just made brought to my mind that it was not until Reagan made up that chart and showed it to a gentleman whom we were trying very hard to convince of the value of slag control that that particular executive opened his eyes and began to let us do many things that he had not allowed up to that time.

H. J. HAND (written discussion).—The author wishes to express his gratitude to both Dr. Johnston and Mr. Dodge for their constructive discussion of the paper. The thought expressed by Mr. Dodge cannot be overemphasized—that with large amounts of data one may not be able to detect true differences or trends, owing to "averaging out" variable conditions. Data must be classified into rational subdivisions for foolproof conclusions. If that has been done, conclusions developed from statistical study are as reliable as those developed in the laboratory, perhaps even more so, for they are directly applicable to operating conditions.

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* Research Engineer, Bethlehem Steel Co.

[10] F. G. Norris: Significance of Slag Control. Unpublished.

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Diffusion of Carbon from Steel into Iron

By Leonard C. Grimshaw,* Member A.I.M.E.

Diffusion of carbon from gases into iron has been the object of much research, because of its long recognized importance in carburizing processes, but the direct diffusion of carbon from steel into iron has received relatively little attention. Because of the increasing use of clad metals in industry, direct diffusion from steel into iron is becoming of practical importance. Therefore, the object of this investigation was to study the diffusion of carbon from several different kinds of steel directly into relatively pure iron, realizing that elements in the steels other than carbon might influence the rate of carbon diffusion.

The previous work on diffusion of carbon into iron has been considerable, and includes many reports in foreign languages. This work has recently been well reviewed by Mehl[1] and Krynitsky,[2] and the reader is referred to their excellent bibliographies.

Methods of Study

There are two main methods by which the direct diffusion of carbon from steel into iron may be studied. In one method, steel is first decarburized in part, and diffusion of carbon then allowed to take place from the steel into the decarburized steel. This method is open to two serious objections: (1) the decarburized steel is not iron, but contains elements such as manganese, silicon, chromium or tungsten, which may be an essential part of the steel under study, and which may seriously influence the diffusion of carbon into the decarburized area; (2) there is from the start of diffusion an unknown carbon-concentration gradient between the steel and the decarburized area.

Another method, which possesses neither of these disadvantages, is to study diffusion from steel into a thick plating of electrolytic iron. Here the chief difficulty is to secure an electrolytic deposit of iron upon steel without introducing an oxide film at the interface that will interfere with diffusion. The author is able to deposit iron upon any kind of steel without introducing an oxide film at the interface, so that diffusion of elements from the steel into the iron is free to proceed unhindered.

Since diffusion takes place in measurable amount only when heat is applied, there is no unknown carbon-concentration gradient at the beginning of the diffusion experiment.

General Procedure

The method of iron-plating the steels is the same as that used by the Latrobe Electric Steel Co. in the making of welds in their clad products, and has previously been described in considerable detail.[3,4] Briefly, the iron is deposited from a Fischer-Langbein solution composed of 3 to 4N ferrous chloride, 6N calcium chloride, and 0.01N free hydrochloric acid, upon a steel surface wet with hydrochloric acid and entirely free from oxide film.[5,6]

Bars of various kinds of steel were given a thick electrolytic coating of iron by this method. Samples cut from these iron-plated bars were held for various lengths of time at different temperatures so that measurable diffusion could take place. So that these samples would be in suitable condition for a study under the microscope of the diffusion that had taken place, they were prepared as suggested by J. H. Whiteley in a recent paper.[7] Whiteley demonstrated that a very small amount of carbon in iron could be observed easily when the iron was heated for 2 min. at 1560° F. (850° C.), quenched, and etched carefully in Le Chatelier and Dupuy's cupric reagent.* Carbon in concentrations between 0.02 and 0.04 per cent shows as white etching areas of martensite in a dark background of ferrite. We followed Whiteley's instructions for using this reagent, and found it very valuable. In addition to showing clearly carbon between 0.02 and 0.04 per cent, the reagent has the advantage of also etching considerably higher-carbon iron into definite structural constituents, which may be observed. Then, after removing the copper by light buffing, one is able to re-etch in nital and find the same place again under the microscope. The low-carbon areas are now less clearly seen, but the areas of higher carbon content are clearly defined with the more familiar nital etch.

Experimental Procedure

The steels used for this investigation are listed in Table 1. The electrolytic iron deposited usually analyzed: C, 0.015 per cent; Si, 0.00; Mn, 0.00; S, 0.014; P, 0.010; Cr, 0.06; Ni, 0.05; Cu, trace. There are also traces of other elements. It is believed that the carbon in this iron is for the most part in the form of occluded particles picked up from those in suspension in the plating solution. It has never been observed as affecting the microstructure. Chromium, nickel and copper come from the mild-steel plates used as anodes. Manganese and silicon do not deposit.

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* Alcohol (95 per cent), 100 c.c.; water, 10 c.c.; copper chloride, 1 gram; picric acid, 0.5 gram; hydrochloric acid, 1 to 3 c.c.

Bars of the steels listed in Table 1 were ground so as to remove all surface decarburization, and finished about ⅞ in. square. They were electrolytically pickled until free from oxide film, and while wet with hydrochloric acid were placed in the iron-plating bath and given a plating

TABLE 1.—*Analyses of Steels Used*

Steel	Composition, Per Cent								
	C	Si	Mn	Cr	W	V	Co	Mo	Ni
A	1.13	0.35	0.26	0.08					
B	0.95	0.32	1.68	0.22					
C	1.10	1.02	0.32	1.05	1.27	0.25		0.58	
D	0.74	0.25	0.30	4.15	17.74	1.11	0.08		0.15
E	0.73	0.23	0.31	4.16	17.80	1.78	12.33	0.87	0.33
F	2.15	0.47	0.52	13.16					0.55

45 to 50 thousandths of an inch thick. The iron-plated bars of steel were then prepared for heat-treating and subsequent polishing in the following way.

Upon one iron-plated face of each bar was clamped a ⅞ by ¼-in. bar of mild steel, and the plated steel and mild steel were then arc-welded together along their edges. It was determined that the effect of this arc welding did not extend very far into the two corners of the iron-plated steel, so that there was at least ½ to ⅝ in. of iron-plated surface enclosed under the ⅞ by ¼-in. mild steel that was quite unaffected by the arc welding, and suitable for experimental work. The object of this step was twofold: first, the mild-steel bar protected the surface of the electrolytic iron from oxidation during heat-treatment, and, second, it protected the edge of the specimen during polishing without interfering with subsequent etching.

For heat-treatment, a piece about 1½ in. long was cut from such a prepared bar and placed in a furnace already at the desired temperature. It came quickly up to heat, was held the required length of time, and quenched in oil. Preparation for microexamination of the diffusion that had taken place was the next step. In order to avoid the surface effect of the diffusion heating, the 1½-in. long sample was cut in half with a hard rubber wheel. Very little air had been able to get between the iron-plated steel and its cover of mild steel, because the two lay closely face to face, and by cutting the sample in halves we had completely avoided end effect.

One half of the sample thus obtained was placed in a furnace at 1560° F. (850° C.) and held at heat for 2 to 3 min., then quenched in water. This treatment, necessary for microexamination, erased all traces of heating by the hard rubber cut-off wheel, and gave a surface only

slightly oxidized, which required very little grinding to remove it before polishing. Care was taken not to temper the sample during grinding and polishing.
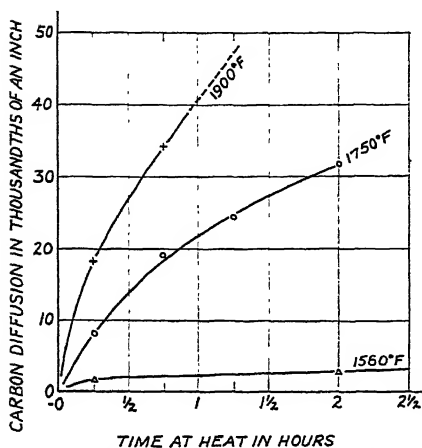
FIG. 1.—CARBON DIFFUSION IN STEEL A.   FIG. 2.—CARBON DIFFUSION IN STEEL B.
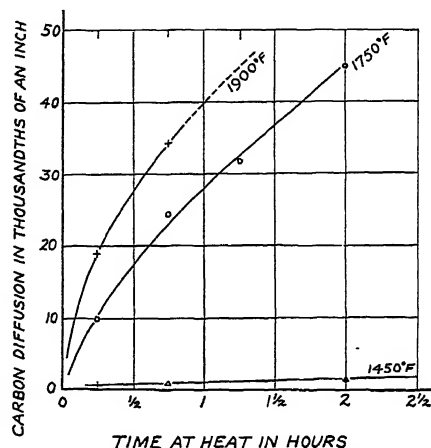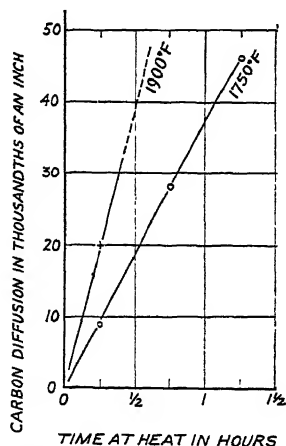
FIG. 3.—CARBON DIFFUSION IN STEEL C.   FIG. 4.—CARBON DIFFUSION IN STEEL D.
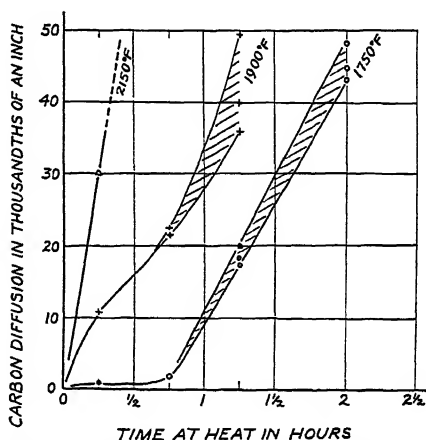
It will be seen from the experimental results that the additional diffusion that could take place during 2 to 3 min. at 1560° F. was of negligible amount.

MEASUREMENT OF DIFFUSION

The greater part of the results is recorded in the form of graphs (Figs. 1 to 6). The distance, in thousandths of an inch, traveled by carbon in concentrations of 0.02 per cent, is plotted against the time in hours during which the specimen was held at the temperature indicated

for each curve. Results of diffusion at some lower temperatures that took place in periods of time greater than 2 hr. are not shown on the graphs because of lack of space, but are recorded in the text.

Figs. 7 and 8 are photomicrographs showing the diffusion that had taken place from steel A at 1900° F. after $\frac{1}{4}$ and $\frac{3}{4}$ hr., respectively. They are typical of the appearance after diffusion at higher temperatures of the three low-alloy steels. The original steel-iron interface is indicated by the line marked 0.0 in.; the steel is below this line, and the electrolytic iron is above it. Distances from the original steel-iron interface are marked in inches to allow easy observance of the amount of diffusion that
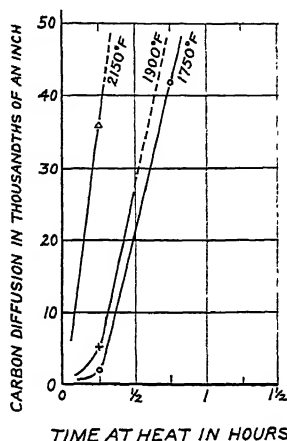
FIG. 5.—CARBON DIFFUSION
IN STEEL E.
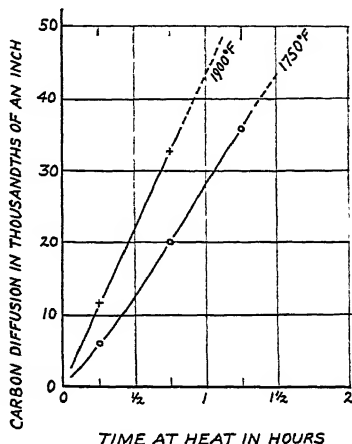
FIG. 6.—CARBON DIFFUSION IN
STEEL F.

took place. All diffusion measurements were made by projecting such structures as Figs. 7 and 8 upon the ground glass of the microscope, and measuring with a scale. At a magnification of 125 diameters, each thousandth of an inch on the specimen measured $\frac{1}{8}$ in. on the ground glass of the microscope, so that accurate measurements could easily be made.

In some cases, diffusion was more difficult to measure. Fig. 9 shows the diffusion in a sample of steel D after $\frac{3}{4}$ hr. at 1900° F. Here it will be seen that a few isolated grains of 0.02 per cent carbon in martensite have diffused over 0.020 in. It is this maximum diffusion that is recorded in the graphs. Three samples were used for each time and temperature, usually with closely checking results, but for steel D poor checks were obtained because of this arbitrary method of measurement, and so results on the graph of Fig. 4 are shown for all three samples. Similar erratic results were obtained for steels A, B and C at 1450° F.

Fig. 10 shows steel A after 2 hr. at 1900° F. Here diffusion has long before reached the edge of the electrolytic iron 0.045 in. thick. This figure is included to compare the cupric with a 2 per cent nital etch.
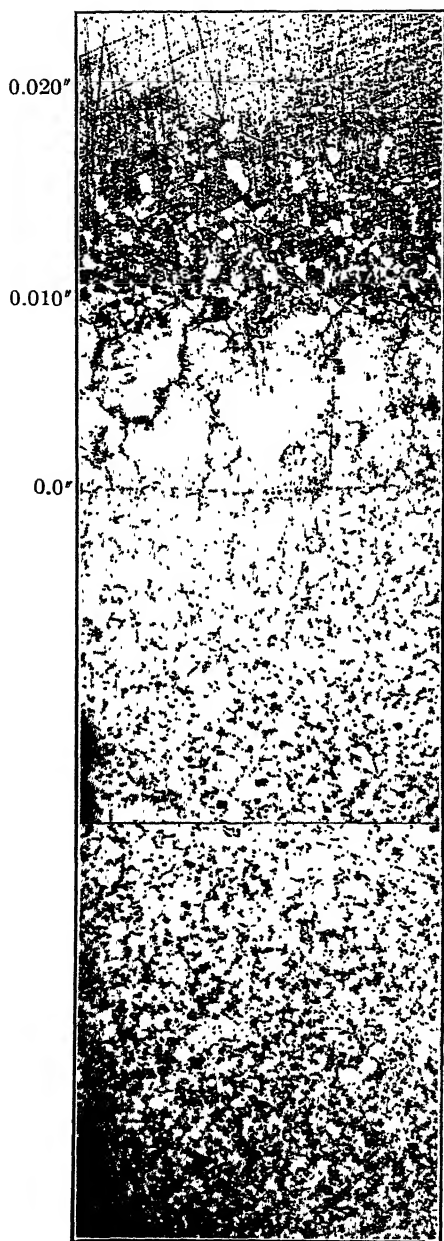
FIG. 7.—STEEL A HELD AT 1900° F. FOR ¼ HOUR, OIL-QUENCHED, THEN AT 1560° F. FOR 3 MINUTES, WATER-QUENCHED. Cupric etch.

Original magnification 125; reduced ⅙ in reproduction.

Notice how much more clearly the lowest-carbon areas are defined with the cupric reagent than with nital.

When carbon diffusion had reached the edge of the electrolytic iron by the next time the structure was observed, the diffusion curve was recorded as a broken line on the graph. These broken-line curves are not entirely supposition, because the carbon content at the edge of the electrolytic iron could be estimated with fair accuracy. In Fig. 10 the time of diffusion was 2 hr., which is too long for such an estimate to be made, but after 1¼ hr. the carbon clearly appeared to have just reached the edge, and is so recorded as a broken line in the graph for steel A, Fig. 1.

RESULTS

As already stated, most of the results are recorded in the graphs of Figs. 1 to 6.

At 1450° F. (790° C.) diffusion of carbon from steel A into the electrolytic iron is very slow, and somewhat erratic in its progress. After 4 hr. at this temperature carbon in concentrations of 0.02 per cent has traveled 0.002 in., and as far as 0.01 in. in isolated places in the same sample. At 1450° F. diffusion of carbon from steel B is also very slow: 0.001 in. in ¾ hr., 0.002 in 2 hr., and 0.003 in. in 6 hr. This shows the effect of the lowering carbon-concentration gradient as diffusion proceeds. At 1450° F., steel C shows the same results as steel A, while steels D, E and F show

no carbon diffusion. At 1560° F. (850° C.), steel A shows faster

and less erratic carbon diffusion than at 1450° F., but the rate slows down as the carbon-concentration gradient is lowered by diffusion (Fig. 1). Fig. 11 shows the appearance under the microscope of a sample of steel A held 15 min. at 1560° F., and it will be observed that recrystallization has taken place in the electrolytic iron. This is probably due to the formation of austenite. First carbon diffuses into alpha iron at 1560° F., and then at the saturation concentration the alpha iron transforms into austenite. At this temperature, the rate of diffusion seems to be essentially dependent upon the diffusion of carbon into alpha iron, as the limiting position of the carbon seems to coincide exactly with the edge of the columnar grains. This rate of carbon diffusion in alpha iron is greatly influenced by the concentration gradient.

Steels B and C were not tested at 1560° F. Steels D, E and F showed no diffusion after 6 hours.

At 1750° F. (955° C.) the electrolytic iron is in the gamma phase, and the graphs show that considerable carbon diffusion takes place in all the steels. The rate increases as the alloy content of the steel is greater, as in steels A, B and C. Steel D, an 18-4-1 high-speed steel, contains carbon combined as stable carbides, and it is interesting to observe that ¾ hr. is required before carbon diffusion starts at

0.030″

0.020″

0.010″

0.0″
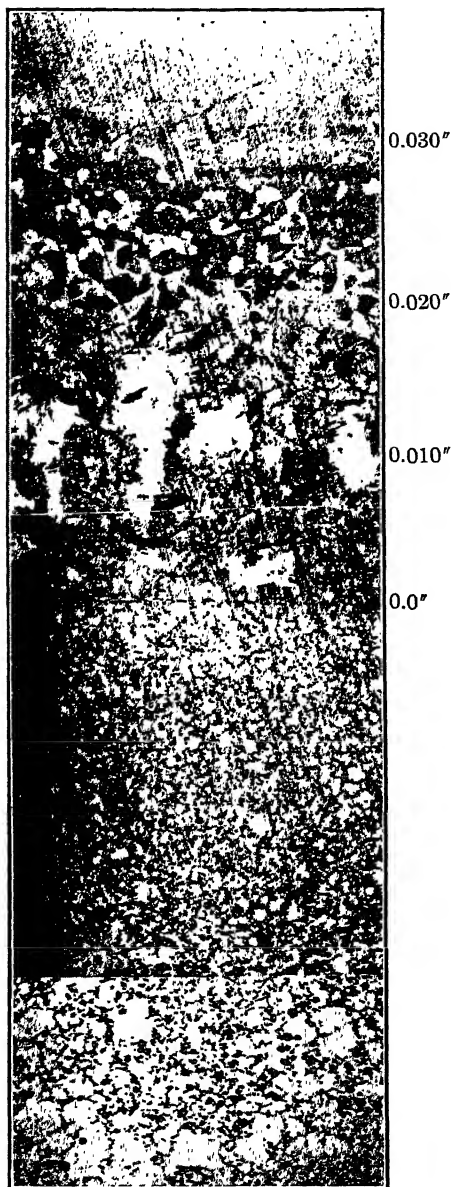
Fig. 8.—Steel A held at 1900° F. for ¾ hour, oil-quenched, then at 1560° F. for 3 minutes, oil-quenched. Cupric etch.

Original magnification 125; reduced ⅓ in reproduction.

a fast rate, and that thereafter the rate is the same as that of steel C. (Slight discrepancy between results for three check samples is shown by shaded areas in Fig. 4, steel D.)   Steel E, a high-speed steel containing 12 per cent cobalt, shows little carbon diffusion in $\frac{1}{4}$ hr., then a very rapid rate.

Both steels D and E contain carbon in stable carbide form, and both show hesitancy in starting diffusion on this account, but diffusion takes place much more rapidly in steel E.   Steel E is known to be much more
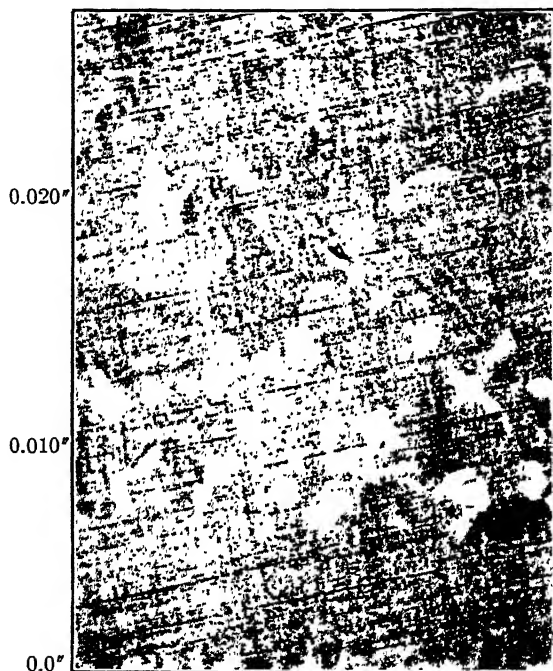
FIG. 9.—STEEL D HELD AT 1900° F. FOR $\frac{3}{4}$ HOUR, OIL-QUENCHED, THEN AT 1560° F. FOR 3 MINUTES, WATER-QUENCHED.   × 125.
Cupric etch.

susceptible to decarburization than steel D in all commercial heat-treatments, and the author believes that there is some property of cobalt that accounts for both rapid decarburization and rapid carbon diffusion from high-cobalt steels.

At 1750° F , carbon diffusion from steel F begins promptly, and proceeds at a uniform rate that is the same as that from steel D, after the latter steel has been held at heat at least $\frac{3}{4}$ hr.   Unlike steel D, not all the carbon of steel F is held in stable carbide form; some of it is free to start diffusing through gamma iron at the beginning.

Attempts were made to study carbon diffusion from some low-carbon stainless steels, but it was found that where all the carbon was in the

form of chromium carbides the chromium diffused as fast as the carbon, or faster, and another etching technic would have to be used to measure it. In steel F, chromium had diffused 0.004 in. after $1\frac{1}{4}$ hr. at 1750° F. in sufficient amount to prevent copper depositing from the cupric reagent,
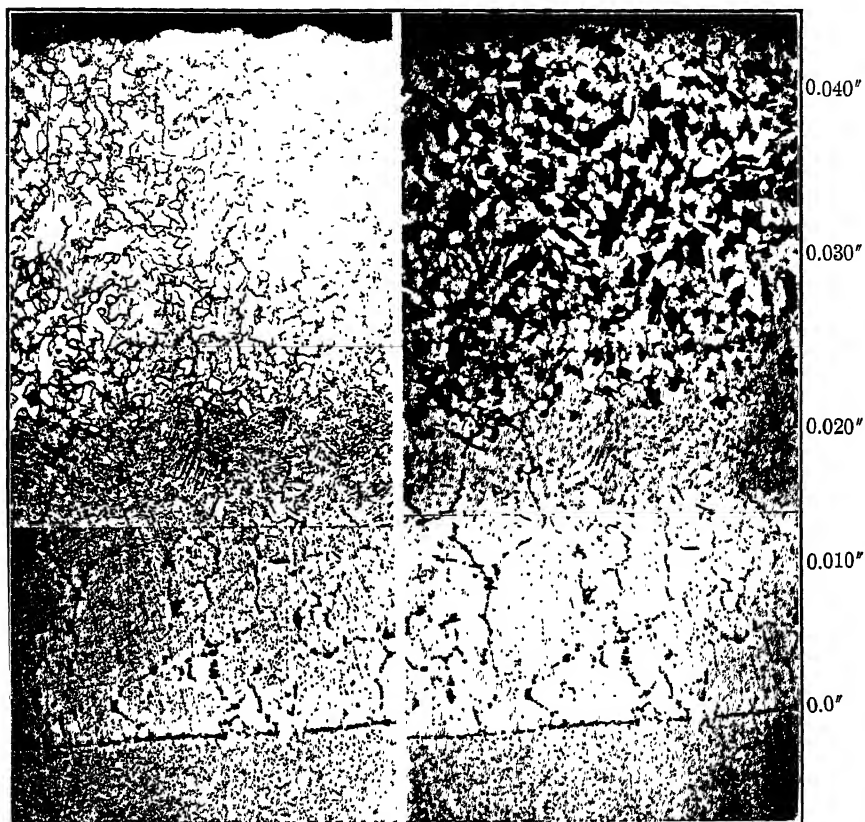
FIG. 10—STEEL A HELD AT 1900° F. FOR 2 HOURS, OIL-QUENCHED, THEN AT 1560° F. FOR 3 MINUTES, WATER-QUENCHED.
2 per cent nital etch on left, cupric etch on right.
Original magnification 125; reduced ⅓ in reproduction.

but the free carbon had far outdistanced this chromium and could be observed with the cupric reagent.

The results for all steels held at 1900° F. are plotted on the graphs. It was possible to hold steels D and E at 2150° F. without "burning," and these results are also plotted.

SUMMARY AND CONCLUSIONS

Electrolytic iron was deposited upon six different steels, and diffusion of carbon from these steels into the electrolytic iron was observed and measured.

It was found that the rate of carbon diffusion from steel into iron increases with temperature. However, this increase in the rate of diffusion is not a function of temperature alone, but is most influenced by the phase of the steel and of the iron at any temperature.

As the temperature is raised to the point where the steel is in the gamma phase, while the iron remains in the alpha phase, carbon diffuses
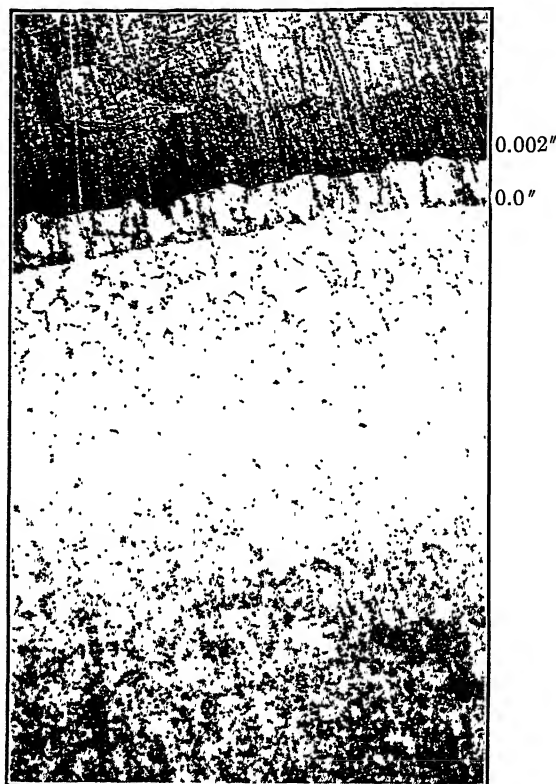
FIG. 11.—STEEL A HELD AT 1560° F. FOR ¼ HOUR, WATER-QUENCHED. × 125.
Cupric etch.

slowly into the alpha iron, and when saturated with carbon the alpha iron changes to gamma iron. Diffusion into alpha iron is greatly influenced by the concentration gradient.

At higher temperatures, where both the steel and the iron are in the gamma phase, diffusion is much faster, and increases in rate as the temperature is raised, although it is very little influenced by the carbon-concentration gradient.

Alloys in the steel influence the rate of carbon diffusion from steel into iron. The addition of small amounts of alloying elements that do not combine with all of the carbon to form stable carbides increases the rate of

carbon diffusion. When the carbon is in the form of stable carbides in the steel, time is required, even at temperatures where the iron is in gamma phase, for the carbides to diffuse into the gamma iron, and there break down and allow carbon to go into solution and diffuse rapidly.

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DISCUSSION

(R. S. Williams presiding)

R. S. WILLIAMS,* Cambridge, Mass.—Mr. Grimshaw, did you do any work with the clad steels? The boundary between the two metals would be quite different from the boundary between electroplated steel.

L. C. GRIMSHAW.—Yes, I have studied diffusion in clad steels. Last May I had published some photomicrographs and explanatory notes that showed diffusion between several steels used for cladding and two steels used for backing material (*Metals Progress*, May 1937). But that kind of diffusion was so complicated that I could draw no conclusions as to exactly what had happened: I could only show the results as photomicrographs. In clad steels diffusion of several elements takes place in opposite directions. It was because of this that I decided to simplify the problem by studying diffusion from different kinds of steel, in one direction only, into an iron that contained no elements that might influence the diffusion.

P. A. E. ARMSTRONG,† New York, N. Y.—Although this excellent paper is not particularly directed to stainless steel of the 18-8 type, a few words concerning intergranular corrosion due to carbon migration in the light of this paper are relevant.

We see here that chromium in some instances diffuses more rapidly than carbon from the chromium carbide in a given steel. The widely held theory, which I cannot accept in its entirety, explaining intergranular corrosion in 18-8 on the basis of migration of carbides to the grain boundaries and resultant depletion of chromium in the zones about the carbides, can be reviewed on the basis that these depleted zones do not occur and that chromium diffuses quickly enough to prevent this occurring, equalization therefore taking place.

* Professor of Physical Metallurgy, Massachusetts Institute of Technology.
† Latrobe Electric Steel Co.

Incidentally, my tentative explanation is that the crystal skin, whatever it may be, is affected by the form, phase or composition and heat-treatment, which sets up various intensities of potential and polarity differences. This, in the presence of the necessary electrolyte, causes solution to take place, or localized corrosion. The carbides of themselves, not dissolving very rapidly, are an accompaniment, not the cause, even though they may be an aggravation.

Clad stainless steel, of either the straight chromium or 18-8 type, that has had a layer of electrolytic iron interposed during its manufacture, prevents almost entirely the migration of carbon either from the backing of mild steel, say not over 0.30 carbon, or from the stainless face into the iron layer. It might be thought a layer of silver, copper or nickel would be necessary. The inexpensive and highly effective layer of electrolytic iron does the trick. The chromium diffuses into the electrolytic iron at temperatures within its gamma phase and before the carbides have time to migrate from either side of the electrolytic iron. Chromium diffused in the electrolytic iron is in a phase or form that effectually stops or extremely retards the diffusion of carbon, so that during rolling or fabricating the carbon does not go across the weld; and heated in service, I would not expect the carbon to go across. The nickel also presumably diffuses into the iron. Microscopic examination shows a rapid diffusion of chromium of straight chromium steel into electrolytic iron when heated above 1750° F. The same is true of nickel, copper, and chromium-nickel stainless steel. With the latter the proportion of chromium to nickel in such diffusion is not known. The difference in etching effect is most marked, also the grain size.

With copper, the electrolytic iron takes on a reddish color with stringers of more pronounced red running down between the crystal of the electrolytic iron.

I have seen no instances of carbon from the backing going across the electrolytic weld zone and into the stainless steel of any type.

The microscopic observation has always been done at about 30° across the weld to observe as much as possible.

P. H. BRACE,[*] East Pittsburgh, Pa.—Is there any possible way of finding out, except by experiment, what the chance is or time element may be before a carbon element ultimately diffuses through, and is it possible that oxidation at the free surface may take the carbon away as fast as it permeates through the intervening layer of chrome iron? Also, how will such things as Inconel behave, particularly with reference to corrosion and resistance and intense intergranular cracking after prolonged periods of service at temperatures in the neighborhood of 600° C.?

R. F. MEHL,[†] Pittsburgh, Pa.—Mr. Armstrong, was that intervening layer of iron in the alpha condition during the treatment?

P. A. E. ARMSTRONG.—It was alpha and when the temperature was raised, I suppose it got into delta, if you can tell me the difference.

R. F. MEHL.—There is no difference, of course. What temperatures were involved?

P. A. E. ARMSTRONG.—The necessary rolling, 2100° or 2200°.

R. F. MEHL.—The thing I had in mind was this: Carbon cannot diffuse rapidly in alpha iron because of its low solubility and the attendant difficulty of creating a concentration gradient, whereas the rate could be high in gamma iron because the solubility is great.

[*] Consulting Metallurgist, Research Laboratory, Westinghouse Electric and Manufacturing Co.

[†] Director, Metals Research Laboratory, Carnegie Institute of Technology.

P. A. E. ARMSTRONG.—So I had heard, but the facts did not work out that way.

R. F. MEHL.—Chromium might diffuse in alpha iron, whereas carbon would not, but the case could be quite reversed in the gamma field, where carbon diffuses much more rapidly than chromium because it is an interstitial solid solution.

P. A. E. ARMSTRONG.—But I do not think it remains long enough in the gamma phase, because it is so highly diffused by chromium.

R. F. MEHL.—The matter of measuring the diffusion of carbon in some irons has engaged us for some time. Mr. Grimshaw's observations are engineering observations, and very properly he made no attempt to determine actual diffusion coefficients. In fact, the measurement of diffusion coefficients is a difficult task. The only reliable data in the literature for the rate of diffusion of carbon in gamma iron are those obtained by Pashke, who welded bar ends of two pieces of steel, one with high carbon and one with low, that had been carefully machined, and after diffusion machined off layers for analysis, thus establishing a carbon concentration curve. All of Bramley's work is quite untrustworthy. His work on the rate of diffusion of carbon is qualitative and not quantitative because his mathematical methods were untrustworthy.

The diffusion of carbon in gamma iron has rather broad metallurgical interest, as we know that alloy steels are used chiefly because they are more sluggishly reactive than plain carbon steels. This sluggishness originates partly in the effect of the alloying element on the rate of diffusion of carbon in austenite and in the inherently slow rate of diffusion of the alloying elements themselves. Since, in a manganese steel for example, manganese associates itself preferentially with cementite in the formation of pearlite, it is thus necessary that both carbon and manganese diffuse when pearlite is formed; nickel thus associates itself with the ferritic phase and therefore must also diffuse. In analyzing the rates of reaction in alloy steels, the diffusion not only of carbon, but nickel, manganese, etc., must be considered. Any real analysis of the rates of reaction in steel on the basis of rates of diffusion requires the determination of at least two diffusion coefficients.

There are some interesting facts about pearlite in connection with this problem. If an attempt is made to evaluate the effect of diffusion coefficients, it is seen immediately that as pearlite is formed at lower and lower temperatures the interlamellar spacing becomes less and less. If the interlamellar spacing becomes less, the copper and nickel and manganese do not have so far to diffuse, so that not only must the change in the rate of diffusion with temperature be considered but also the variation in the distances over which diffusion must take place. Interestingly enough, whereas the diffusion coefficient varies exponentially with temperature, becoming very small at low temperatures, the interlamellar spacings also vary logarithmically with temperature in the same way, so that the two temperature coefficients are mutually opposed and mutually cancel, at least in part.

L. C. GRIMSHAW.—In answer to both Dr. Brace and Dr. Mehl, I must go a little beyond the scope of this paper, because both of them asked questions about steels clad with stainless iron or with 18-8. I have iron-plated and heat-treated pieces of 16 per cent chrome iron and 18-8 in the same manner as the steels reported in this paper. But Whiteley's method of etching to show carbon diffusion was useless with these stainless steels because chromium diffused as fast or faster than any carbon. The high-carbon high-chromium steel recorded in the paper contained so much carbon that some of it diffused faster than the chromium, and could be seen and measured. But the 10 points of carbon in stainless irons never diffused faster than the chromium.

Iron-plated 16 per cent chrome iron and 18-8 when held at 2100° F. both showed an enormous grain growth in the electrolytic iron adjacent to the stainless iron. I supposed that the pure electrolytic iron was in the gamma phase, and a large amount of chromium quickly diffused into it, accompanied by very little carbon because of the low-carbon concentration gradient. At 2100° F., once considerable chromium and negligible carbon had diffused into it, might not the gamma iron change to the delta phase? Carbon diffusion from that moment becomes almost impossible. I have no proof of this theory, but the enormous grain size of the chromium-filled electrolytic iron adjacent to the stainless iron would lead us to suspect delta phase.

When we examine a commercial stainless clad steel that has been made in such a way that there is a few thousandths of an inch of electrolytic iron between cladding and backing steel, we never observe that carbon diffuses across the weld. After hot-rolling and annealing, chromium diffuses through the electrolytic iron, and may proceed into the backing steel. May not this chromium-filled electrolytic iron be a barrier of delta phase at high temperatures, through which carbon cannot pass? Later, the clad steel may be held at temperatures where this zone is gamma phase, but then the diffusing carbon would tend to be arrested there to form chrome carbides.

It must also be remembered, when we fear contamination by carbon of these commercial clad stainless steels, that usually there is almost the same carbon content in the stainless iron and mild steel backing.

Dr. Mehl's comments upon the influence that other elements may have upon the rate of carbon diffusion are especially valuable coming from an acknowledged leader in this field. They emphasize what was observed in this paper: that we can hardly simplify conditions too much when we study diffusion from commercial steel. Every element in the commercial steel may have its effect on the diffusion rate of the element being studied. Since any element may diffuse with the element being studied, we must use a pure iron as the medium that they diffuse into. If we use a commercial mild steel as the solvent, as has so often been done, we become hopelessly confused.

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Constitution of Iron-chromium-manganese Alloys

By C. O. Burgess* and W. D. Forgeng*

Despite the increasing interest in and the technical importance of iron-chromium-manganese alloys, very little published information is available regarding their constitution. F. M. Becket's paper[1] in 1930 represents the first correlated effort in the field of these alloys. The paper served particularly to draw attention to the commercial possibilities of iron-rich alloys containing chromium and manganese in balanced proportions. The duplex structure of alloys within the commercial range was briefly discussed, but exposition of their structural constitution was necessarily limited because the physical properties and corrosion resistance of the alloys were the main subjects of the paper.

Both prior to and following the publication of F. M. Becket's paper, and at his instigation, an extensive investigation of the constitution of iron-chromium-manganese alloys of commercial purity was in progress at the Union Carbide and Carbon Research Laboratories, Inc. The present paper is based on the results of that investigation. In the last few years, investigations covering various portions of this alloy system have also been made in Europe. W. Koester briefly mentioned the effect of annealing on chromium-manganese steel[2] and later[3] constructed approximate sections of the iron-chromium-manganese equilibrium diagram.

M. Schmidt and H. Legat[14] even more recently studied this system, and their article and conclusions are of interest as representing an entirely independent study of a number of iron-chromium-manganese alloys.

Koester's sections are shown in Fig. 1. The figures summarize the effect of manganese additions to iron alloys containing 5, 10, 15 and 20 per cent Cr as well as the effect of increasing chromium content on iron alloys containing 3, 8, 20 and 30 per cent Mn. These diagrams, within their composition limits, substantiated in some measure the results of our investigation. However, in our work some differences as regards the position of the mixed alpha-gamma fields were found as compared to Koester's work, and we were able to detect the presence of

complex phase changes in the solid state in alloys with certain concentrations of chromium and manganese. The occurrence of such phase changes in some iron-chromium-manganese alloys has been independently verified by F. Bruehl[4] and by Schmidt and Legat.[14] For alloys containing 30 per cent Cr and more than 10 per cent Mn, Bruehl noted that on long annealing the alpha solid solution decomposed into austenite and a
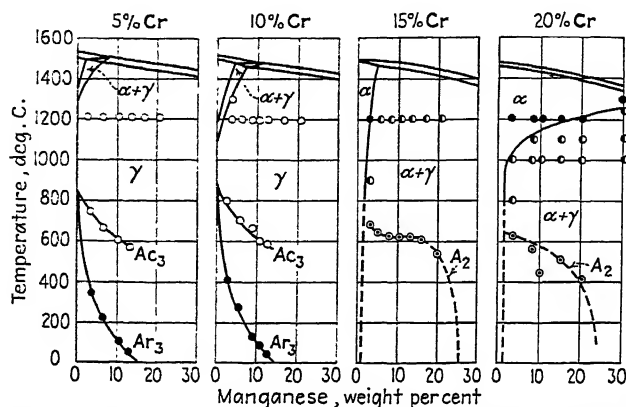
FIG. 1a.—SECTION THROUGH IRON-CHROMIUM-MANGANESE PHASE DIAGRAM AT CONSTANT CHROMIUM CONTENTS.   (KOESTER.)
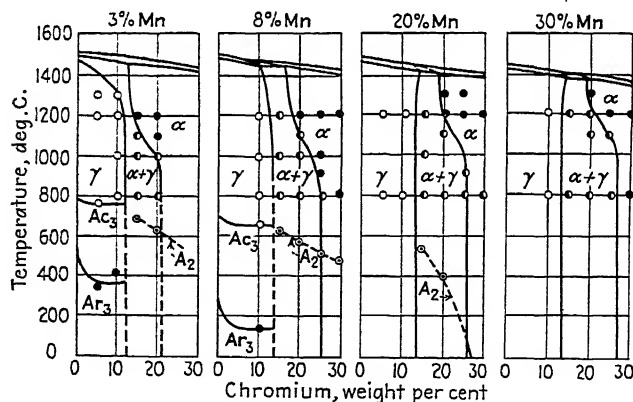
FIG. 1b.—SECTIONS THROUGH IRON-CHROMIUM-MANGANESE PHASE DIAGRAM AT CONSTANT MANGANESE CONTENTS.   (KOESTER.)

compound that he identified as FeCr. This mechanism, however, does not agree with our conception of the phase changes that take place in such alloys, particularly in regard to precipitation of austenite. In other words, we were not able to find any evidence of gamma precipitation from the alpha phase in such alloys, and, furthermore, some of the evidence pointed to an explanation other than compound formation for such phase changes.

MATERIALS USED IN INVESTIGATION

In the course of this investigation, numerous low-carbon iron-chromium-manganese alloys were prepared, of which 43 were selected as illustrating significant points in the ternary system. The alloys are mainly in the iron-rich section of the system and cover a range of chromium contents up to approximately 60 per cent, and manganese contents up to 50 per cent. Their analyses are given in Table 1. Their locations on a ternary composition diagram are shown in Fig. 2.

All the alloys were prepared in high-frequency furnaces, the weight of an individual heat being either 6 or 10 lb. The basic raw materials
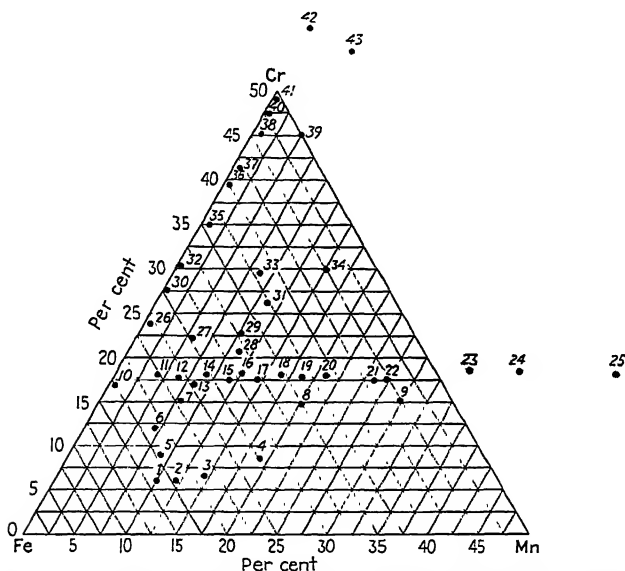
FIG. 2.—LOCATION OF EXPERIMENTAL HEATS IN TERNARY SYSTEM.

employed were Armco iron, low-carbon ferrochromium, low-carbon ferromanganese and silicon metal. In a number of cases commercial electric-furnace heats of similar analysis to the heats shown in the table were also prepared and were found to possess properties and structures similar to those of the experimental heats.

The alloys were submitted to heat-treatments, which included quenching from various temperatures up to 1150° C. and homogenizing by holding at 1000° C. for extended times followed by slow cooling.

DETERMINATION OF PHASES PRESENT IN THE ALLOYS AT VARIOUS TEMPERATURE LEVELS

All the alloys, both as forged and after submission to various heat-treatments, were examined microscopically. The findings in this exam-

TABLE 1.—*Analysis of Experimental Alloys*

Code No.	Composition, Per Cent			
	Cr	Mn	C	Si
1	6.05	10.23	0.10	0.27
2	5.98	12.10	0.10	0.25
3	6.55	14.52	0.05	0.41
4	8.41	18.70	0.11	0.52
5	9.31	9.17	0.08	0.36
6	12.08	7.16	0.05	0.15
7	14.77	8.12	0.07	
8	14.60	20.48	0.12	0.55
9	14.70	29.81	0.12	0.42
10	16.97	0.35	0.05	
11	17.93	3.72	0.08	0.59
12	17.47	6.48	0.06	0.32
13	17.19	8.35	0.11	0.24
14	17.80	8.90	0.07	0.33
15	17.66	11.62	0.09	0.30
16	17.92	12.45	0.06	0.27
17	17.52	14.53	0.06	0.28
18	17.88	16.53	0.05	0.27
19	17.50	19.08	0.05	0.23
20	17.94	21.00	0.10	0.30
21	17.87	26.48	0.06	0.30
22	17.48	27.04	0.08	
23	18.53	35.19	0.12	0.31
24	18.51	40.41	0.13	0.38
25	18.45	49.87	0.12	0.36
26	23.70	0.53	0.12	0.35
27	22.02	5.34	0.06	0.08
28	20.41	11.00	0.09	0.35
29	22.82	10.00	0.05	0.33
30	27.25	0.63	0.10	0.37
31	26.04	11.08	0.05	0.31
32	30.51	0.57	0.13	0.39
33	29.38	8.35	0.15	0.41
34	30.15	15.27	0.09	0.40
35	35.00	0.70	0.08	0.38
36	39.72	0.62	0.12	0.38
37	41.08	0.49	0.06	0.31
38	44.91	0.78	0.13	0.42
39	44.82	5.34	0.14	0.46
40	47.14	0.62	0.05	0.38
41	48.94	0.71	0.16	0.47
42	58.31	0.78	0.15	0.57
43	59.10	5.31	0.15	0.62

ination were checked against the results of hardness and magnetic tests
as well as X-ray diffraction analysis of the alloys.   From information so
obtained on alloys of commercial quality, ternary diagrams representing
isothermal sections of the iron-chromium-manganese system have been
prepared.   These diagrams, as noted previously, cover the constitution
of alloys containing up to 60 per cent Cr and up to 50 per cent Mn.   The
ternary diagrams are to a large extent self-explanatory, but it is necessary
to describe, even though briefly, the experimental findings on which these
diagrams are based.

Considering first a relatively simple section—that is, equilibrium at
1000° C. as shown in Fig. 3—it may be seen that the iron-manganese por-
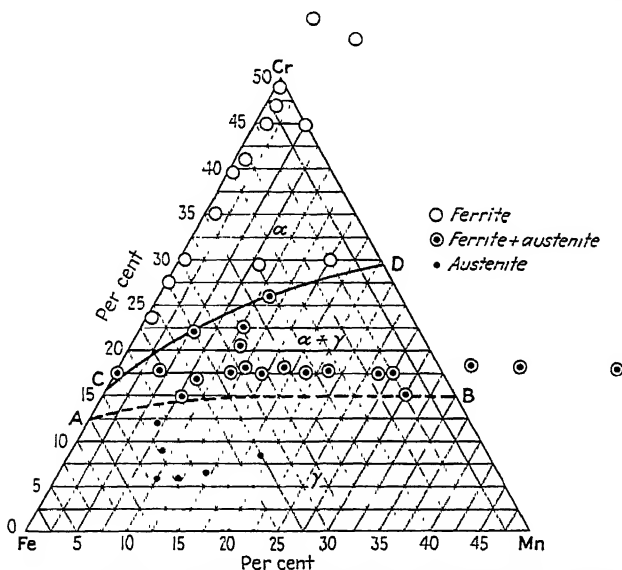
FIG. 3.—PHASES PRESENT AT 1000° C. FROM MICROSTRUCTURE.

tion of the diagram is occupied entirely by the gamma phase.   This
would be expected from the well-known gamma-forming tendency of
manganese[5] when added to iron.

In the iron-chromium region much information[6] is again available,
the gamma-phase field in alloys of low carbon content being replaced by
a mixed alpha-gamma field, by addition of approximately 12.5 per cent
Cr, and the gamma phase in the alpha-gamma field being replaced
entirely by the alpha or body-centered phase when the chromium reaches
approximately 15 to 17 per cent.   Considering next alloys containing
both chromium and manganese, it might be expected that the presence
of manganese, because of its tendency to preserve gamma iron, would
extend the austenite loop considerably and with increasing manganese
render completely austenitic alloys with considerably higher chromium

contents than 12.5 per cent. However, examination of the ternary alloys shows that only a slight rise in the permissible chromium content for a completely austenitic alloy occurs even with a substantial increase in manganese content (line AB in Fig. 3), and when the chromium exceeds approximately 15 per cent it is no longer possible to render the low-carbon alloys completely austenitic, even though the manganese is increased to 50 per cent. A marked widening of the alpha-gamma field does occur, however, with increase in manganese, and a type of duplex structure consisting of alternate grains of ferrite and austenite is stabilized when
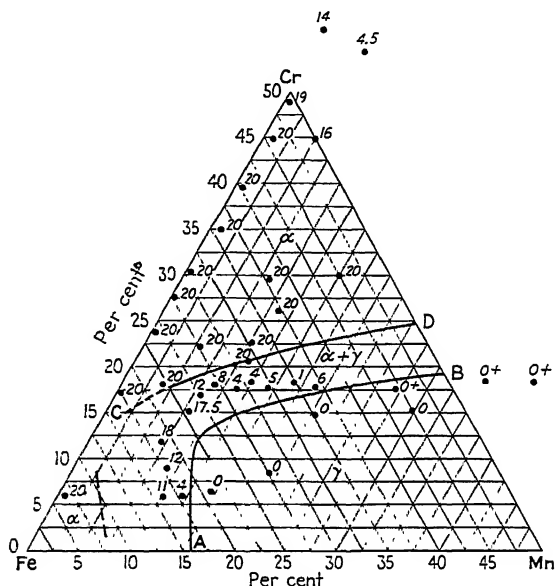
FIG. 4.—RELATIVE MAGNETISMS OF ALLOYS QUENCHED FROM 1000° C.

the manganese reaches or exceeds 4 per cent. It also becomes possible with further increase in manganese content to readily retain these austenite grains undecomposed in a ferrite groundmass. In addition to the widening of the alpha-gamma field, any increase in manganese at a constant chromium content increases the relative quantity and stability of austenite in the alloy without completely destroying the last traces of ferrite. This will be illustrated in the subsequent discussion of Fig. 7 dealing with homogenized alloys. By metallographic examination it was also possible to fix accurately the limit of the alpha and alpha-gamma fields as shown by line CD in Fig. 3.

The results of magnetic tests on the same series of iron-chromium-manganese alloys after rapid cooling from 1000° C. are shown in Fig. 4. The small numerals represent the force necessary to separate the specimen and the poles of a small, powerful permanent magnet as measured by the extension in inches of a light spring. If these relative values are used to

define the alpha, alpha-gamma and gamma fields as microstructure was used in Fig. 3, it will be noted that the alpha-gamma field is considerably contracted as compared to the former diagram. This is to be expected
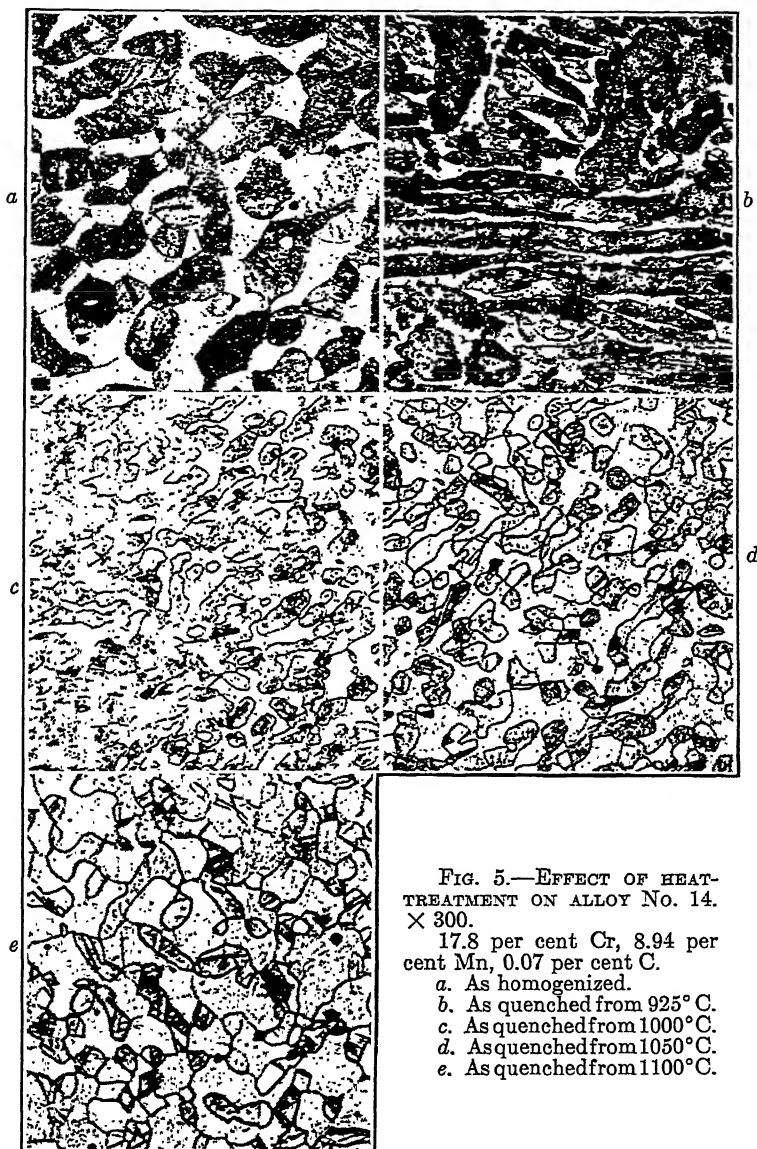
FIG. 5.—EFFECT OF HEAT-TREATMENT ON ALLOY No. 14. × 300.

17.8 per cent Cr, 8.94 per cent Mn, 0.07 per cent C.
a. As homogenized.
b. As quenched from 925° C.
c. As quenched from 1000° C.
d. As quenched from 1050° C.
e. As quenched from 1100° C.

because in the magnetic method of testing the appearance of small amounts of austenite in an alpha matrix or the presence of very small amounts of ferrite in an austenite groundmass are not readily detected.

It is further to be expected that austenite will not be retained in alloys low in manganese and chromium, accounting for the "knee" in the line AB. Considering these factors the magnetic measurements afford a satisfactory confirmation of the microscopic observations.

Of interest in the consideration of the effect of heat-treatment of alloys containing 6 to 14 per cent Mn, and lying in the alpha-gamma region, is the fact that the austenite grains that would suffer partial decomposition on slow cooling can be stabilized by quenching from a sufficiently high temperature. This is clearly shown in Fig. 5, which is a series of
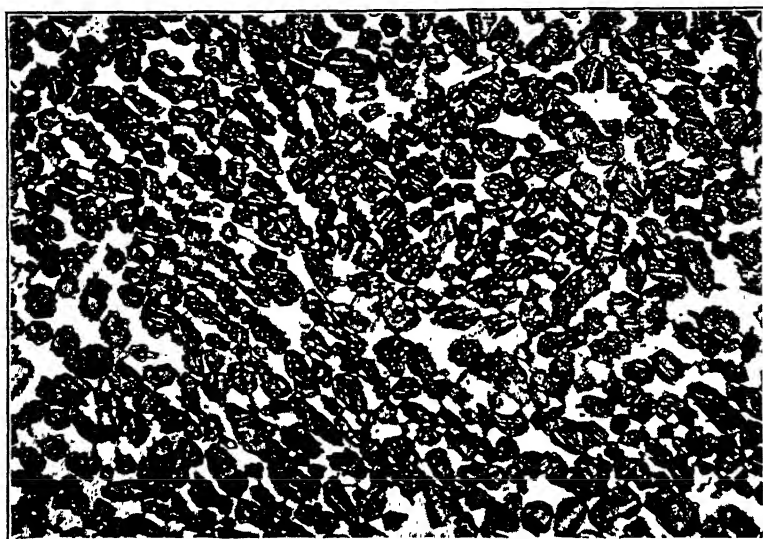
FIG. 6.—ALLOY No. 14. QUENCHED FROM 1050° C. AND DRAWN AT 750° C.   × 300.
17.8 per cent Cr, 8.94 per cent Mn, 0.07 per cent C.

photomicrographs illustrating the changes occurring in heat No. 14, containing 0.07 per cent C, 17.80 per cent Cr and 8.94 per cent Mn, on quenching from 925°, 1000°, 1050° and 1150° C. It is evident that with increase in quenching temperature an increase in the amount of the ferritic constituent takes place with an accompanying contraction and stabilization of the original austenite grains. The explanation of this behavior is clear if we consider the critical points exhibited by an alloy in this range of analysis. From the observed critical points, down to approximately 1040° C., the alloy consists predominantly of alpha (delta) iron. Therefore, when the alloy is held above approximately 1050° C. the alpha-iron grains increase at the expense of the austenite grains and the austenite grains are only slightly decomposed on quenching. The increase in stability of the austenite grains is probably due to concentration of carbon in these areas, accompanying the increase in alpha iron. The increase in alpha iron is less marked at 1050° and 1000° C. than at 1150° C., as these

former temperatures undoubtedly approximate or are just below the delta transformation point. The alloy treated at 925° C., on the other hand, lies entirely in the zone of maximum austenite formation, and therefore the austenitic grains are more diffuse and less stable in the alloy on quenching from this temperature and the amount of free alpha iron is at a minimum.

In the lower-manganese alloys, considerable decomposition of the austenite retained by quenching can be induced by heating at 750° C., as may be seen in Fig. 6, which illustrates the structure of alloy No. 14 after quenching from 1050° C. and drawing 1 hr. at 750° C.
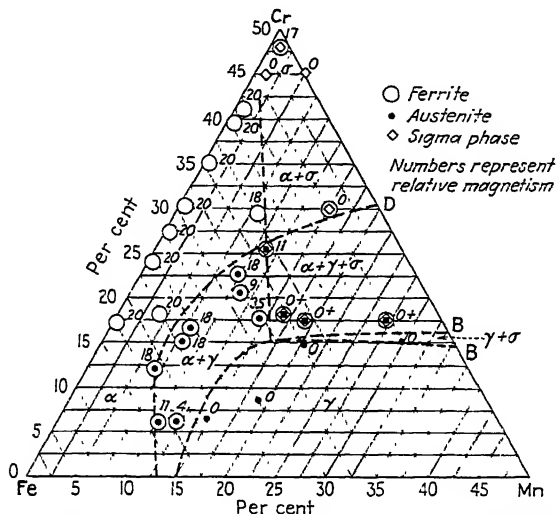
FIG. 7.—CONSTITUTION OF ALLOYS SLOWLY COOLED FROM 1000° C.

In Fig. 7 is illustrated the constitution of iron-chromium-manganese alloys after holding for periods of up to 15 hr. at 1000° C. followed by slow cooling. Two marked differences are evident on comparison of Fig. 7 with Fig. 3. In the first place, the alpha field extends the full length of the iron-chromium side of the system from 0 to about 41 per cent Cr. This results from the instability of the austenite in the low-manganese alloys on slow cooling. The second difference is the appearance of a new constituent designated as sigma, which forms only in the ferritic phase of the alloys in the alpha or alpha-gamma regions. This phase departs widely in character from either the austenite or ferrite modification, but does closely resemble in character the phase that has been assigned the formula FeCr by investigators of the iron-chromium system. It can be readily identified by methods that will be described more fully in a later section.

In addition to symbols identifying the phases, the relative magnetisms of the individual alloys in inches of extension are shown as numerals

No. 10.   0.35 per cent Mn.
× 100.

No. 11.   3.72 per cent Mn.
× 300

No. 13.   8.35 per cent Mn.
× 300.

No. 16,   12.45 per cent Mn.
× 300.

No. 18.   16.53 per cent Mn.
× 300.

No. 21.   26.48 per cent Mn.
× 100.

No. 23.   35.19 per cent Mn.
× 100.

No. 25.   49.87 per cent Mn.
× 100.
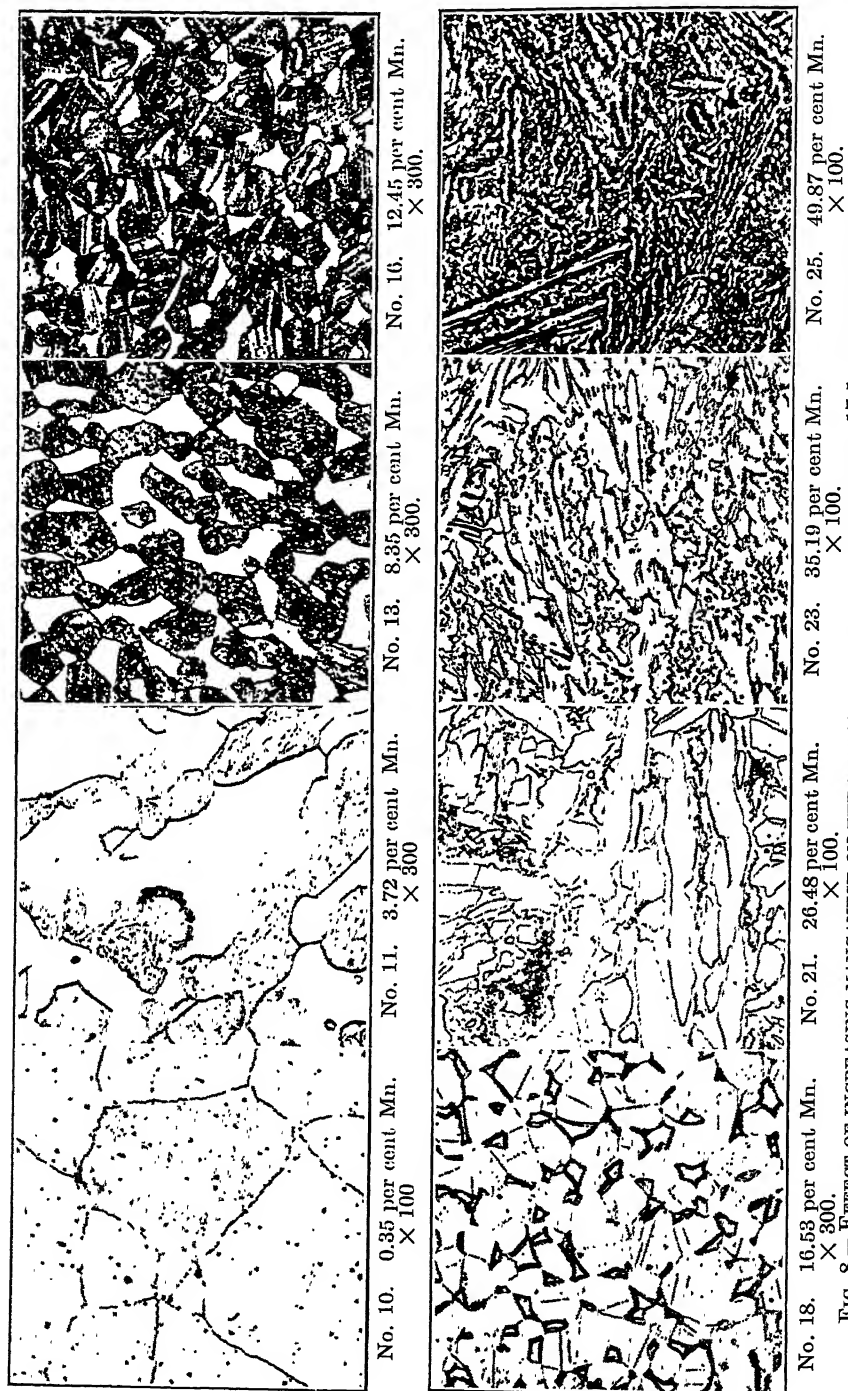
FIG. 8.—EFFECT OF INCREASING MANGANESE ON THE MICROSTRUCTURE OF HOMOGENIZED 17.5 PER CENT CHROMIUM ALLOYS.

No. 6.   12.08 per cent Cr.   No. 7.   14.77 per cent Cr.   No. 14.   17.80 per cent Cr.   No. 33.   20.38 per cent Cr.
Constant 8 per cent manganese content.

No. 15.   17.66 per cent Cr.   No. 28.   20.41 per cent Cr.   No. 29.   22.82 per cent Cr.   No. 31.   26.04 per cent Cr.
Constant 11 per cent manganese content.
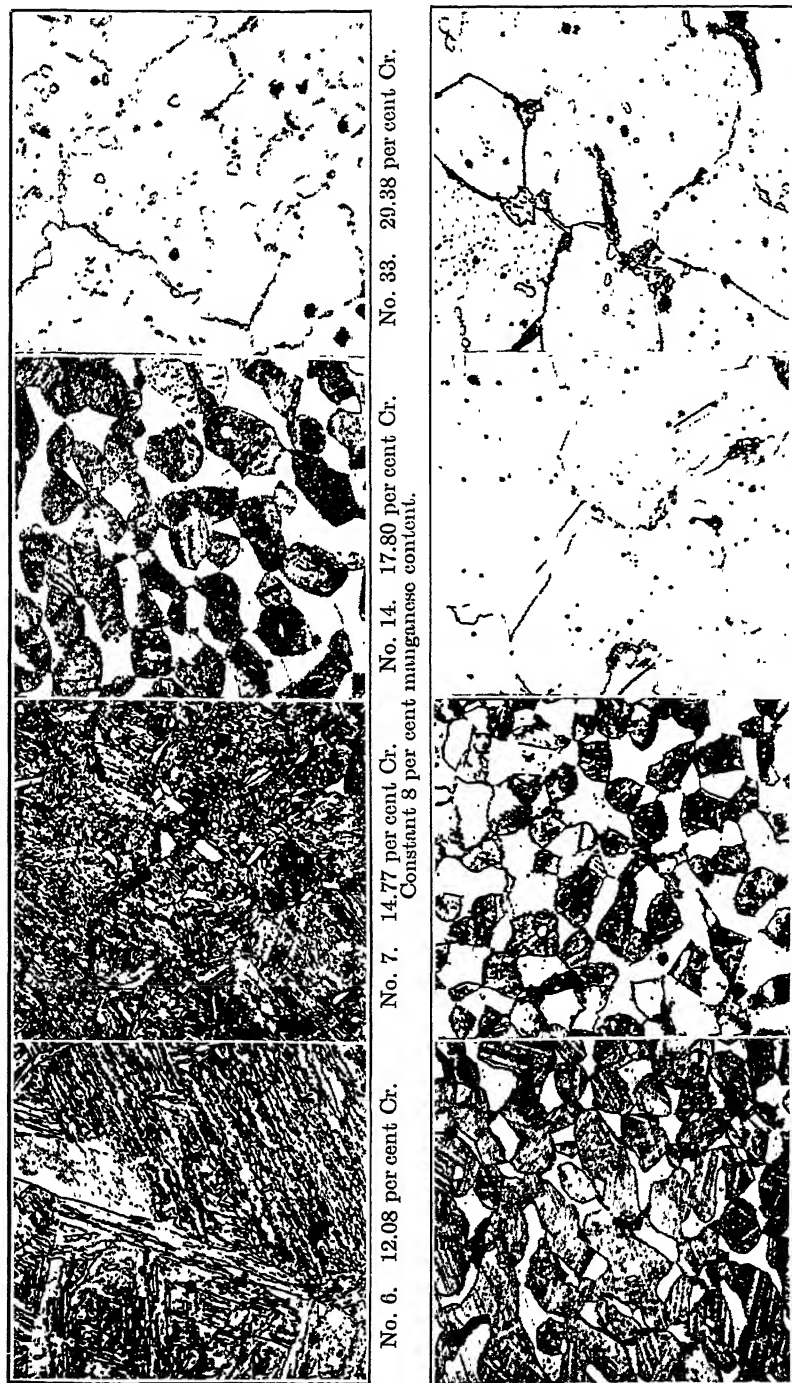
Fig. 9.—Effect of increasing chromium content on the microstructure of 8 per cent and 11 per cent manganese alloys—300 ×.

associated with the symbols in Fig. 7. These values are consistent with the observed microstructures.

By way of illustration of the type of structural changes that are recorded in Fig. 7, a series of photomicrographs of homogenized alloys are shown in Figs. 8 and 9. In Fig. 8 the effect of increasing manganese content on the microstructure of alloys with a constant chromium content (approximately 17.5 per cent) is clearly evident. With the lowest

FIG. 10.—ALLOY NO. 34. FURNACE-COOLED FROM 1000° C.   × 250.
30.15 per cent Cr, 15.27 per cent Mn.

manganese content the microstructure is mainly ferritic. As the amount of manganese rises, areas of decomposed austenite appear and increase at the expense of completely ferritic portions of the alloys. Finally, with sufficient manganese, a stabilization of the austenite takes place. At about 16.5 per cent Mn the decomposition of the ferrite to a new phase may be noted. This phase persists and increases in amount up to a content of approximately 50 per cent Mn.

In Fig. 9 is considered the effect of increasing chromium contents in alloys with constant manganese contents (8 and 11 per cent). As may be

most clearly followed in the 8 per cent Mn series, the homogenized alloys possess a Widmanstätten structure until the chromium content increases to approximately 15 per cent, at which point small crystals of ferrite appear as a stable constituent in the groundmass. This ferritic phase increases until it occupies 50 per cent of the groundmass as the chromium content rises to approximately 17.50 per cent. With approximately 30 per cent Cr present, an 8 per cent Mn alloy is seen to be completely ferritic. At the 30 per cent Cr level an increase in manganese does not cause the formation of austenite but instead renders the ferritic structure comparatively unstable. As a result, the ferrite of a 30 per cent Cr, 15 per cent Mn alloy is readily converted to the sigma phase on furnace cooling. This is illustrated in Fig. 10, a photomicrograph of the furnace-

TABLE 2.—*Effect of Manganese on the Formation Temperature of Sigma Phase*

Alloy No.	Composition, Per Cent		Maximum Temperature at Which Sigma Is Formed, Deg C.
	Cr	Mn	
32	30.51	0.57	a
33	29.38	8.35	800
34	30.15	15.27	900+
35	35.00	0.70	700
36	39.72	0.62	800
38	44.91	0.78	850
39	44.82	5.34	950+
41	48.94	0.71	850+

a None formed in finite time.

cooled alloy No. 34. The dark matrix in this figure is the sigma phase resulting from decomposition of pre-existing ferrite. The elongated white areas are residual ferrite, and the small white rounded particles are carbides. The same alloy can be completely converted to sigma phase if it is held at 700° to 800° C. for several hours.

The transformation of ferrite to sigma was studied in greater detail at the 45 per cent Cr level. A 44.91 per cent Cr, 0.78 per cent Mn alloy required 7 hr. at 700° C. for complete transformation from ferrite to sigma. On the other hand, alloy No. 39, which is a 44.82 per cent Cr, 5.34 per cent Mn alloy, could be completely converted to the sigma phase in an hour. This transformation can be followed very readily by magnetic measurements, since the sigma phase is nonmagnetic while the chrome ferrite in such an alloy is, of course, strongly magnetic.

Examination of this and other iron-chromium-manganese alloys has shown that manganese has a remarkable accelerating action on the ferrite to sigma transformation. Furthermore, the temperature range

in which the sigma phase is stable is appreciably widened by the presence of manganese, as shown in Table 2.

This influence of manganese apparently resides in its ability to render unstable the ferrite of the very high-chromium alloys, and when present in sufficient amount, the residual ferrite of alloys in the alpha-gamma field. The amount of manganese necessary to readily produce sigma decreases as the chromium content rises to 45 per cent.

Fig. 11 is an isothermal section of the ternary system at 650° C. This diagram was deduced from microscopic examination of alloys
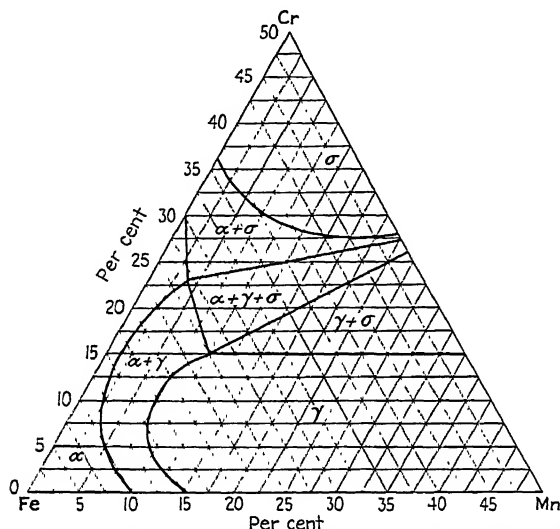
FIG. 11.—ISOTHERMAL SECTION OF THE IRON-CHROMIUM-MANGANESE SYSTEM AT 650° C.

annealed for very long periods of time at temperatures between 600° and 1000° C. At 650° C. the ferrite, either in the high-chromium alloys or in the mixed alpha-gamma field with over a certain percentage of manganese, is not stable and is replaced totally or in part by the sigma phase.

CHARACTERISTICS OF SIGMA PHASE

In a search for etching reagents that would reveal small amounts of the sigma phase, two methods were found to be quite satisfactory. One required a light etch in a 10 per cent aqueous solution of hydrochloric acid and examination with reflected polarized light; the second involved the use of a modified Murakami's reagent. The latter is prepared by mixing 30 grams each of potassium hydroxide and potassium ferricyanide with 60 c.c. of water. It must be made up fresh and used at boiling temperature.

When a specimen that has been converted completely to the sigma phase is etched in a 10 per cent solution of hydrochloric acid in water

and viewed with ordinary illumination, it appears very similar to an unconverted alloy of the same composition except for the presence of
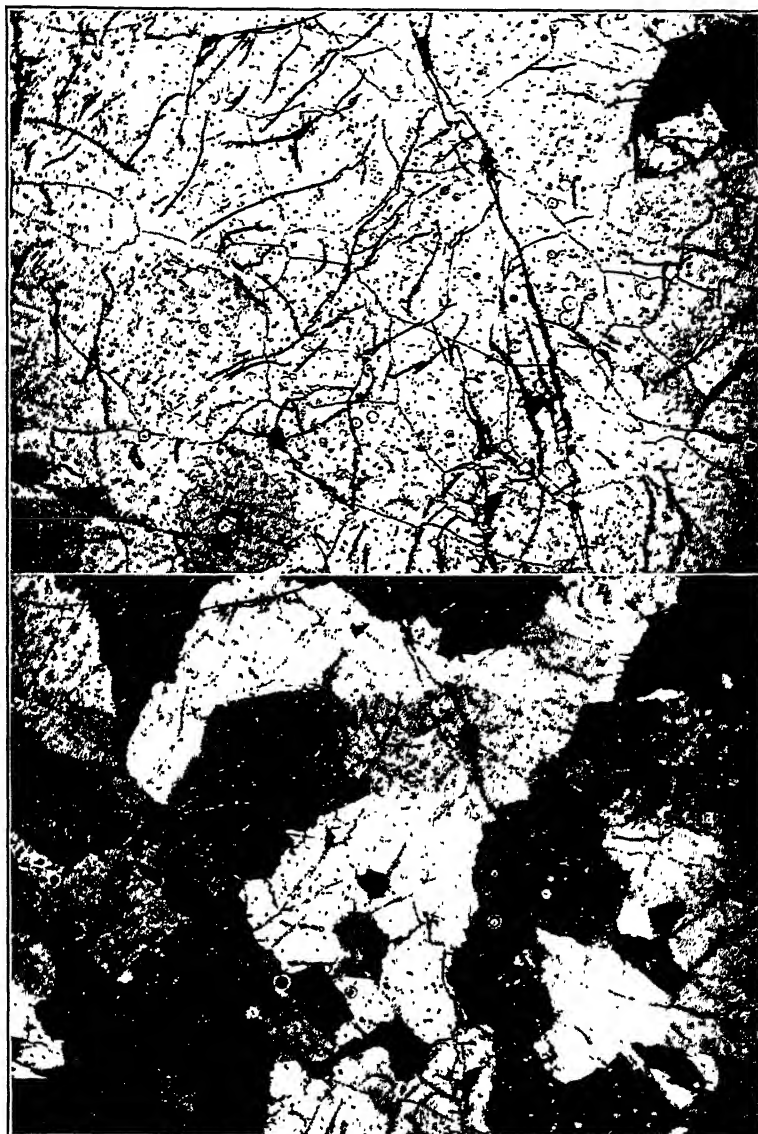
FIG. 12.—ALLOY NO. 39 HELD 2 HOURS AT 700° C.   ETCHED WITH 10 PER CENT HCL.
ORDINARY ILLUMINATION.   × 100.
44.82 per cent Cr, 5.34 per cent Mn.
FIG. 13.—SAME FIELD AS FIG. 12 VIEWED BETWEEN CROSSED NICOLS.   × 100.

numerous cracks (Fig. 12).   Between crossed nicol prisms this specimen is decidedly anisotropic, the grains becoming alternately bright and dark
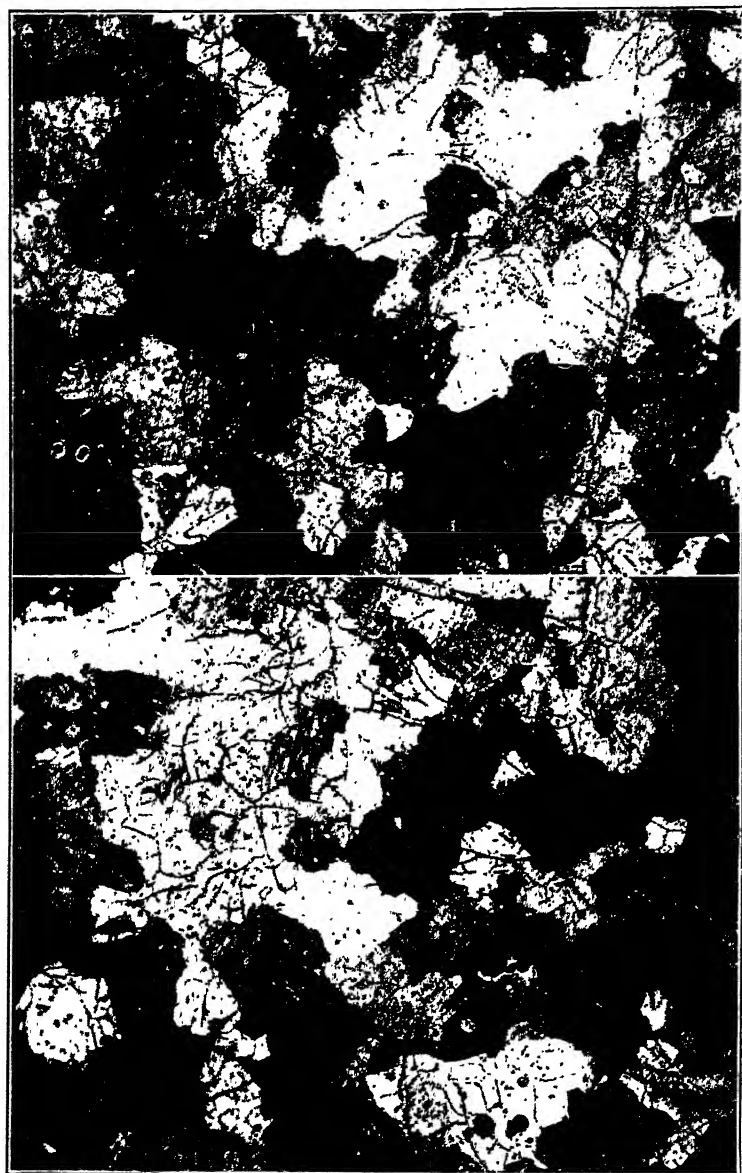
FIG. 14.—ALLOY No. 39 HELD 2 HOURS AT 700° C. ETCHED WITH 10 PER CENT HCL. × 100.
a. Typical field between crossed nicols.
b. Same field after rotation of nicols through 90°.

as the specimen is rotated. Fig. 13 is the same field as Fig. 12 as it appears between crossed nicols. In Fig. 14 is shown the manner in which the grains of the sigma constituent alternate from light to dark on rotation of the specimen through 90°. In this figure and the previous figure the grain boundaries of the sigma phase revealed by the use of polarized light do not follow the grain boundaries of the pre-existing ferrite as outlined by the carbide particles, but instead form a new grain pattern. This behavior resembles that associated with allotropic trans-
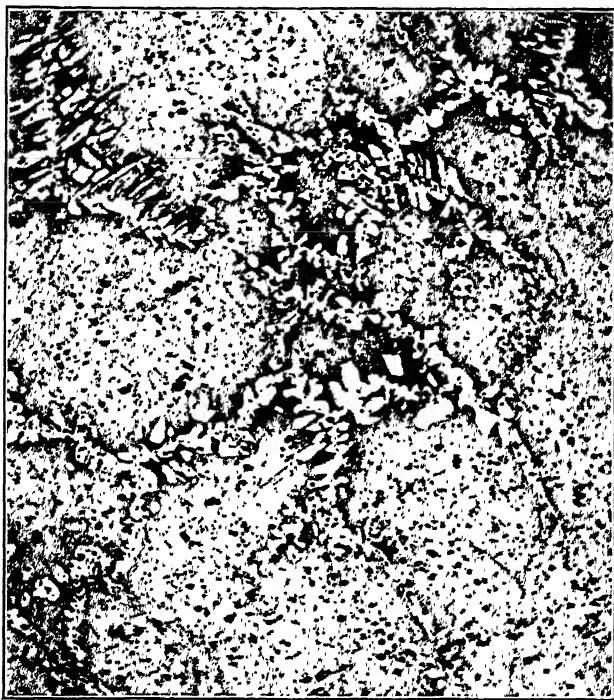
FIG. 15.—ALLOY NO. 33 HELD 100 HOURS AT 800° C. ETCHED WITH ALKALINE POTASSIUM FERRICYANIDE.   X 100.
29.38 per cent Cr, 8.35 per cent Mn.

formation rather than the formation of a compound as postulated by Bruehl.[4] For this reason, throughout the present paper the new phase has been given the designation of sigma at variance with Bruehl, who assigned the formula FeCr to the constituent found in his limited range of alloys.

Also, in view of the variable composition of the sigma phase—the manner in which manganese, nickel, silicon, etc., may be substituted in that phase—the designation of the phase as a compound would seem to be a misnomer. Instead, it is possible that the phase is the result of an allotropic transformation of a highly saturated ferrite, other elements as

well as chromium contributing to this saturated condition. Such an explanation of the mechanism in our present state of knowledge is purely speculative. It is felt, however, that an exhaustive X-ray study of the relative crystal structures of high-purity ferritic alloys before and after the formation of the sigma phase may yield a conclusive answer to this problem.

The use of the modified Murakami's reagent permits a ready distinction between ferrite and sigma, the two constituents being revealed in contrasting colors. Fig. 15 is an example of this type of etch on a sample that consists chiefly of ferrite; i.e., alloy No. 33, containing 29.38 per cent Cr and 8.35 per cent Mn, after being held at 800° C. for 100 hr. The sigma constituent was actually light blue and the ferrite was yellow. Fig. 16 is a photograph of two specimens of the same alloy, No. 39, con-

a   b
FIG. 16.—ALLOY No. 39. ETCHED WITH AQUA REGIA. × 2.
44.82 per cent Cr, 5.34 per cent Mn.
a. Held 20 hours at 1000° C. and water-quenched.
b. Held 1 hour at 1000° C. and very slowly cooled.
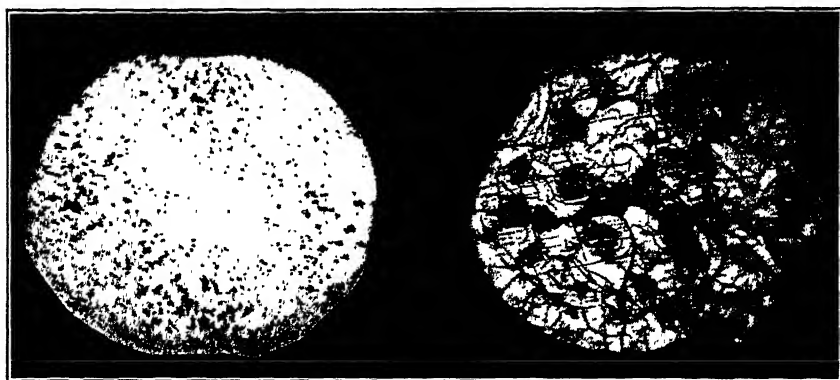
taining 44.82 per cent Cr and 5.34 per cent Mn. The one on the left was held at 1000° C. for 20 hr. and water-quenched, while the one on the right was held at that temperature for only one hour and cooled very slowly. The slowly cooled alloy consists entirely of sigma and has a very much larger grain size than the quenched alloy. It was found that the grain size in such an alloy was dependent upon the temperature at which the transformation was allowed to take place. The grain size is coarser at higher temperatures of conversion.

The cracks in the converted specimen are often associated with the sigma phase, and are the result of a pronounced volume change accompanying the ferrite to sigma transformation.

The microhardness of the sigma phase was found to be in the range of 3906 to 5917 K. The carbide Cr_4C present in the alloy had a microhardness of 2600 to 3906 K while the ferrite had a microhardness of 657 to 977 K.

HARDNESS DETERMINATIONS

The Brinell hardnesses of the alloys after water-quenching from 1000° C. are recorded in Fig. 17. In the same figure, the hardness values of furnace-cooled alloys are shown in parentheses. The greatest differences between the hardness values of the quenched and furnace-cooled specimens occur in the alpha plus sigma and sigma regions, which are delineated in Fig. 7. This is because the major part of the groundmass of these alloys is converted to the sigma phase. It should be stated that the Brinell hardnesses recorded for the sigma-phase alloys undoubtedly
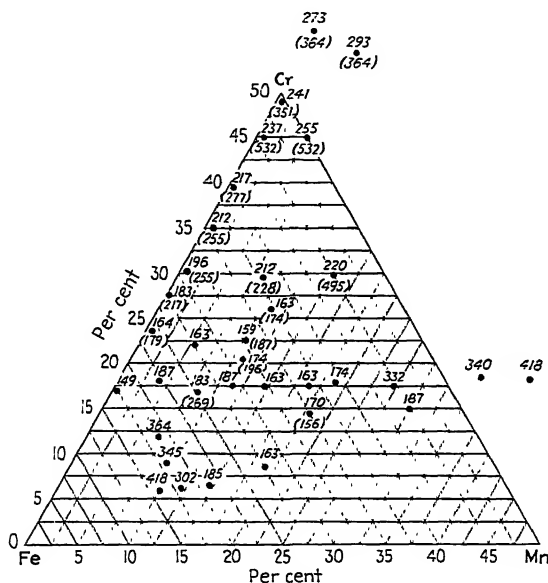
FIG. 17.—BRINELL HARDNESS VALUES OF ALLOYS WATER-QUENCHED FROM 1000° C. Values of furnace-cooled alloys in parentheses.

fall considerably below the true hardness values, since the brittle character of the alloys makes it impossible to obtain accurate determinations by conventional methods. The hardness of this phase as determined by means of the microcharacter is considered more reliable.

DIFFRACTION ANALYSIS OF ALLOYS

X-ray diffraction studies were made of a number of representative alloys after various heat-treatments, especially when the exact identification of phases was difficult by microscopic methods. The results of the diffraction studies served as checks on the microscopic method and in some instances as bases for certain boundaries shown in the ternary diagrams. The phases present in furnace-cooled alloys as determined from their diffraction patterns are recorded in Table 3.

In correlating the results of microscopic and X-ray studies it was found that the first appearance of small amounts of the sigma phase was more readily detected microscopically.

It was established that the crystal pattern of the sigma phase in an alloy containing approximately 30 per cent Cr and 15 per cent Mn was

TABLE 3.—*Results of X-ray Diffraction Analysis*

Alloy No.	Composition, Per Cent		Phases Present after Slow Cooling from 1000° C.
	Cr	Mn	
1	6.05	10.23	Alpha + gamma
3	6.55	14.52	Gamma
6	12.08	7.16	Alpha + gamma
7	14.77	8.12	Alpha + gamma
8	14.60	20.48	Gamma
9	14.70	29.81	Gamma + sigma
10	16.97	0.35	Alpha
14	17.80	8.90	Alpha + gamma
15	17.66	11.62	Alpha + gamma
16	17.92	12.45	Alpha + gamma
19	17.50	19.08	Alpha + gamma + sigma
21	17.87	26.48	Alpha + gamma + sigma
26	23.70	0.53	Alpha
28	20.41	11.00	Alpha + gamma
29	22.82	10.00	Alpha + gamma
30	27.25	0.63	Alpha
31	26.04	11.08	Alpha + gamma + sigma
32	30.51	0.57	Alpha
33	29.38	8.35	Alpha
34	30.15	15.27	Alpha + sigma
35	35.00	0.70	Alpha
36	39.72	0.62	Alpha
38	44.91	0.78	Alpha + sigma
39	44.82	5.34	Alpha + sigma
41	48.94	0.71	Sigma
42	58.31	0.78	Alpha
43	59.10	5.31	Alpha

the same as that of the sigma phase in an alloy containing approximately 49 per cent Cr with low manganese. In view of its complicated nature, it has not yet been possible to interpret the sigma-phase pattern in terms of crystal structure, although it is readily distinguished from the simple patterns of the alpha and gamma phases.

DISCUSSION OF RESULTS

The ternary sections of the iron-chromium-manganese system developed in the present investigation resemble corresponding sections of the

iron-chromium-nickel system. This is to be expected, since manganese, in common with nickel, promotes the formation and stability of austenite in iron-chromium alloys. When added to iron-chromium alloys, however, manganese is much less influential than an equal amount of nickel in creating and preserving a completely austenitic structure. For example, while a low-carbon 18 per cent Cr 8 per cent Ni alloy can be rendered fully austenitic, an 18 per cent Cr alloy of low carbon content in which 8 per cent Mn takes the place of the nickel will not be made completely austenitic by any heat-treatment but will consist of alternate grains of austenite and ferrite. The relatively lower austenite stabilizing power of manganese is immediately apparent in any comparison of the two alloy systems, and in fact it has been recognized[7] that the austenitizing effect of manganese is about half that of nickel.

It should be borne in mind that while the addition of as little as 8 per cent Mn to a 15 per cent Cr alloy will yield a ductile alloy consisting of approximately equal parts of stable austenite and ferrite, the further addition of manganese even up to 50 per cent will not render a low-carbon alloy of this or higher chromium content completely austenitic. This is clearly brought out in the ternary diagrams of the iron-chromium-manganese system shown in this paper.

The sigma phase, which can be developed by suitable heat-treatment in alloys containing sufficient chromium and manganese, undoubtedly bears a close similarity to both the B constituent[8] in iron-chromium-nickel alloys and the "FeCr compound"[9–13] now commonly associated with the iron-chromium system. The approximate limits of composition and temperature within which the sigma phase will form in the iron-chromium-manganese alloys have been systematically determined. Two methods were developed for the ready detection of this phase, one depending on the anisotropic effects shown by the phase when etched in a specified manner, and the second depending on the use of an etching reagent that selectively colors the sigma phase. From the characteristics of the sigma phase and its variable composition, the opinion is advanced that the sigma phase results from an allotropic transformation of a highly saturated ferrite and is not considered to be an intermetallic compound. Complete saturation may evidently be brought about when either the chromium or the combined chromium and manganese contents of a ferritic phase are in the range of 40 to 50 per cent.

It should be stressed that iron-chromium-manganese alloys containing up to approximately 20 per cent Cr and 12 per cent Mn do not contain the sigma phase as quenched, as forged, or as furnace-cooled, and that extended holding at temperatures below 800° C. is necessary for the development of the phase, and it is doubtful whether the phase can be developed in finite time in alloys containing somewhat lower amounts of manganese and chromium. These latter alloys exhibit an alpha or a

mixed alpha-gamma structure under normal cooling conditions, the quantity of retained austenite or gamma phase naturally increasing with an increase in the manganese content of the alloy.

It is realized that the alloys considered in this investigation are only of commercial quality and contain appreciable amounts of both carbon and silicon. It is felt, however, that the establishment of approximate isothermal sections of the system will stimulate further research and be of value in predicting the phases that can be developed in iron-chromium-manganese alloys.

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The authors wish to express their gratitude to Dr. F. M. Becket and Mr. J. H. Critchett, under whose general direction this investigation was undertaken. They are indebted to the management and staff of the Union Carbide and Carbon Research Laboratories, Inc. for their aid and encouragement, and particularly to Mr. Russell Franks and Dr. A. B. Kinzel. The authors wish to thank Mr. R. H. Dunlap, who rendered valuable assistance in the experimental work, and Dr. Jette and Dr. Foote, of the Columbia School of Mines, who prepared and interpreted certain of the diffraction patterns.

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DISCUSSION

(Cryil Wells presiding)

P. A. E. ARMSTRONG,* New York, N. Y.—My observations concerning the paper by Burgess and Forgeng become relevant only because of the suggestion by the authors that manganese, nickel, silicon, etc., may be substituted in the sigma phase.

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* Latrobe Electric Steel Co.

Whether the extraordinary brittleness that can be produced in these alloys by reheating for a long time to temperatures around about 1400° F., or by very slowly cooling is the result of the sigma phase or due to a very finely divided precipitate plus a very readily observed precipitate, I do not know.

The paper by Schmidt and Legat, referred to by the authors, states that a small amount of nickel improves the physical properties of the chrome-manganese alloys. This I also found to be a fact. They also say that the percentage of silicon in chrome-manganese steel must not be too high because silicon (the same is true of aluminum) acts like a higher percentage of chromium, but to an intensifying degree. I do not find this to be a fact; aluminum acts differently from silicon. Which again leads me towards the tendency to believe that the regrettable hardness in chromium-manganese steels is the result of a precipitate rather than a none-too-well correlated phase, which has been designated here as sigma.

An alloy containing about 20 per cent Cr and 12 per cent Mn, with 2 per cent Al, when quenched from 2100° F. has a Rockwell hardness of C-23, and is strongly magnetic. When drawn to 1400° F. for 15 hr. following the quenching treatment, it is the same hardness, magnetic, and in both instances tough.

An alloy containing about 25 per cent Cr and 6 per cent Mn, 1 per cent Al, as quenched 2100° F.. Rockwell C-16; as drawn 1400° F. for 15 hr., Rockwell C-18 was tough and strongly magnetic with both heat-treatments.

An alloy containing about 25 per cent Cr, 12 per cent Mn, with 2 per cent Al, when quenched from 2100° F. in water, was tough, and Rockwell C-22; strongly magnetic. When similarly quenched and drawn to 1400° F. for 15 hr., had a Rockwell of C-53; was strongly magnetic, but very brittle.

An alloy containing about 25 per cent Cr, 16 per cent Mn, 1.5 per cent Al, when quenched from 2100° F. Rockwell hardness C-23, and strongly magnetic and tough. When similarly quenched and drawn to 1400° F. for 15 hr., had a Rockwell hardness of C-57; strongly magnetic and very brittle. When followed by 1600° F. heat for one hour and air-cooled, the Rockwell hardness was C-21; strongly magnetic.

An alloy containing about 30 per cent Cr, 6 per cent Mn, 1.5 per cent Al, quenched from 2100° F., Rockwell hardness C-20; strongly magnetic, tough. When drawn to 1400° F. for 15 hr., Rockwell C-39; strongly magnetic, very brittle, and had a similar falling off of hardness when followed by 1600° F. for 1 hr. and air-cooled.

An alloy containing about 30 per cent Cr, 12 per cent Mn, 1.5 per cent Al, when quenched from 2100° F. in water, Rockwell C-18; tough and strongly magnetic. Drawn at 1400° F. for 15 hr., air-cooled, Rockwell C-67; strongly magnetic, very brittle. Followed by a 1600° F. draw for 1 hr. and air-cooled, the hardness fell to Rockwell C-20; strongly magnetic.

These melt analyses and data are selected from a large number of experimental heats containing aluminum, and are representative of this series. Therefore it appears that aluminum seems to prevent the formation to a very large degree of the non-magnetic form of the sigma phase, if it exists; hardness is certainly present.

Silicon causes the chrome-manganese alloys to get hard and brittle when similarly heat-treated. The silicon addition, which is about 1 to 3 per cent, or somewhat greater, accentuates the nonmagnetic condition in these alloys.

The alloys of less than 35 per cent Cr with varying manganese forge very well as a whole. Nickel beyond 2 per cent or thereabouts has a tendency to reduce the forgeability. Nickels in the order of about 8 per cent with chromium in excess of about 20 per cent will still permit some of these alloys to get hard; that is, better than Rockwell C-45. They are generally strongly magnetic when quenched, and nonmagnetic when drawn to 1400° F. for 15 hr., but in nearly all instances when given the drawing temperatures are brittle, even though they are generally very tough indeed when quenched.

The addition of other elements such as tungsten and molybdenum does not improve the alloy particularly from the toughness point of view; it increases their hardness slightly. Titanium seems to be more powerful in this respect than the other so-called high-melting-point elements. Titanium does not detract from the toughness of the alloy when quenched, but it does not lessen the brittleness when given the drawing temperature.

Aluminum apparently does not act at all like silicon, in that while it allows hardness to be present the alloys in each instance still remain magnetic. I do, however, have some instances where the lower aluminum alloys have become slightly magnetic. The structures of the alloys as microscopically observed look very similar to those given in the authors' paper.

Ordinary carbons in the order of 0.40 per cent or less do not seem to affect the alloys particularly; they still remain soft when quenched; and where they are capable of being made hard by a long-time draw, perform in much the same way.

It is easier to visualize the peculiar properties of chromium-manganese alloys as a phase change in the alpha iron, but precipitation could easily cause the excessive brittleness of these alloys when reheated to about 1400° F. for a long time or slowly cooled, and it might seem that precipitation rather than a phase change is present when aluminum is added. The hardness would be a very great advantage if it could be obtained without brittleness, as we would then have a very high chromium alloy that could be materially increased in physical properties by simple heat-treatments.

F. M. WALTERS, JR.,* Youngstown, Ohio.—What is the effect of the mechanical properties of the precipitation of more or less sigma?

J. S. MARSH,† New York, N. Y.—Why pick on a polymorphic transformation of the sigma phase?

C. WELLS,‡ Pittsburgh, Pa.—Hicks' diffusion experiments[15] in which chromium was diffused into iron at 1000° C. show that the alpha plus gamma field enclosed in the gamma loop of the iron-chromium diagram should be much wider than is usually supposed, and on this account it is suggested that the line of Fig. 3 might be more accurate if it were lowered towards the left so as to meet the line Fe-Cr at a much lower point (1 per cent Cr or less). This viewpoint is based on the belief that in Hicks' experiments equilibrium was much more closely realized than in those made by the investigators whose results the present authors have accepted.

In Fig. 7 no reference is made to the presence of epsilon (a hexagonal close-packed constituent), which occurs in certain iron-manganese alloys and no doubt in iron-chromium-manganese alloys—at least in those containing a small amount of chromium. It may be that epsilon was not observed because the authors' alloys contain sufficient carbon to suppress the formation of epsilon. Of course, even in the absence of carbon, this constituent may not occur in any of the ternary alloys containing 6 per cent Cr, the lowest chromium content alloy investigated.

E. R. JETTE,§ New York, N. Y.—Upon what evidence has the position in Fig. 11 of the boundary between the alpha plus sigma and sigma phases been based? The authors indicate that this boundary intersects the iron-chromium binary at about 36 per cent Cr, which seems to me too low. As far as I have been able to determine,

* Research Engineer, Youngstown Sheet & Tube Co.
† Associate Editor, Alloys of Iron Research.
‡ Metals Research Laboratory, Carnegie Institute of Technology.
[15] L. C. Hicks: *Trans.* A.I.M.E. (1934) **113**, 163.
§ Associate Professor of Metallurgy, Columbia University.

from a rather small number of experiments, I must confess, this intersection should be closer to 45 than to 36 per cent. This would have a marked effect on the curvature of the boundary and the area of the two-phase region alpha plus sigma.

Another question concerns the evidence for the existence of the cubic carbide Cr_4C, or, as Westgren would prefer, $Cr_{23}C_6$. In certain regions of the iron-chromium-silicon system the only carbide occurring is based on Cr_7C_3, which is trigonal.[16] Because of the complexity of the quaternary system, it would be useful if the authors would state the evidence they possess for the existence of the cubic carbide and the annealing conditions and composition of the alloys in which this phase was found.

C. O. BURGESS and W. D. FORGENG (written discussion).—Mr. Armstrong's observations on the effect of aluminum additions to iron-chromium-manganese alloys are of decided interest. We know comparatively little regarding the influence of additions of a fourth or fifth element on the location of the sigma phase. It may well be, however, that small amounts of aluminum are very effective in stabilizing the magnetic alpha phase in these alloys, so that complete conversion to sigma is not obtained on annealing. Such an explanation would be in conformity with the theory that aluminum acts like a higher percentage of chromium.

We are glad Mr. Armstrong agrees that it is easier to visualize the distinctive properties of the higher chromium-manganese alloys as due to a phase change in the alpha iron. We do not believe that precipitation explains the hardening of these alloys, but rather that the hardness is an intrinsic property of the sigma phase. This appears evident from the fact that continued heating in a range where the sigma phase is stable does not lessen the hardness, as would be expected in a precipitation-hardening mechanism.

In answer to Mr. Walters' question, the sigma phase is extremely hard and brittle. The ductility of an alloy is consequently lowered by the presence of any considerable amount of that phase.

In response to Mr. Marsh's observation, our grounds for assuming that the sigma phase results from an allotropic transformation are briefly that a different grain network results with the formation of sigma from alpha,[17] and that the sigma phase may have a variable composition. Until a clear conception of what constitutes an intermetallic compound is forthcoming, it seems easier to visualize a simple polymorphic transformation of the alpha lattice to a sigma lattice than a chemical combination of the iron atoms with those of chromium and manganese.

Dr. Wells has suggested that the line in Fig. 3 marking the boundary between the alpha plus gamma field and the alpha field be lowered to meet the Fe-Cr side at a lower chromium content, on the basis of diffusion work by Hicks. The actual junction point shown in the diagram is an average of that reported by numerous investigators of the iron-chromium system and is in accordance with the authors' observations. Hicks' work is valuable, without doubt. However, there is sufficient disagreement regarding the interpretation of his results to make an alteration on this basis alone inadvisable. In addition, the temperature employed by Hicks was significantly higher than that considered in Fig. 3, and in order to make use of his data extrapolation would be necessary.

We do not show the epsilon phase in the neighborhood of the iron-manganese line because a special study was not made of this binary system. As noted by Dr. Wells, the iron-manganese alloys under investigation contained a minimum of 6 per cent Cr. Available information indicates that no direct relationship exists between the epsilon phase and the phases detected in the iron-chromium-manganese alloys.

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[16] See page 303 this volume.

[17] A characteristic of allotropic transformation. See Tammann: Textbook of Metallography, 195. New York, 1925. The Chemical Catalogue Co. Inc.

In regard to the comments by Dr. Jette on the position of the boundary line between the sigma and sigma plus alpha fields, we were able to produce about 10 per cent of the sigma phase by holding a 39 per cent Cr alloy at 800° C. When the same alloy was held at 700° C. the amount of the sigma phase increased to a little better than 50 per cent. We made the assumption that at some lower temperature sufficient holding time would have completely converted the alloy to the sigma phase.

The formula Cr_4C was used to designate the carbide in the 45 per cent Cr, 5 per cent Mn alloy, since it was established by Tofaute, Küttner and Buttinghaus on the basis of X-ray patterns that the cubic carbide Cr_4C (or $Cr_{23}C_6$) is the only carbide present in a 45 per cent Cr alloy unless the carbon content exceeds about 3 per cent. In the iron–chromium–carbon system the carbide Cr_4C occurs as a result of a peritectic transformation that involves the trigonal carbide Cr_7C_3. Since the alloy in question contained low carbon, and only 5 per cent Mn, and was thoroughly annealed, it seemed likely to the authors that the formula Cr_4C was a suitable designation.

X-ray Study of Effects of Adding Carbon, Nickel or Manganese to Some Ternary Iron-chromium-silicon Alloys

By Eric R. Jette* and A. G. H. Andersen,† Members A.I.M.E.

The results of an investigation of the ternary system iron-chromium-silicon were reported in 1936 by the present authors.[1] Partly for the sake of theoretical interest, and partly because of the possible commercial importance of these alloys, the present investigation was undertaken to determine the effect of some of the commoner elements likely to occur, deliberately or otherwise, in such alloys if made on a commercial scale. The elements thus added were carbon, nickel or manganese. The alloys studied were, therefore, parts of quaternary systems. This investigation was concerned primarily with the effect of these additional elements on the alpha-iron phase and the boundary between this phase region and the alpha plus sigma two-phase region. The sigma phase is a ternary solid solution based upon the compound FeCr. The work was performed mainly by X-ray methods, but a number of microscopic examinations were also made and are reported.

While isolated alloys in the composition ranges studied may have been discussed in metallurgical publications, no systematic investigation of any assistance to us was found. Of the earlier work, the investigations on the iron-chromium-carbon system and on the chromium carbides by Westgren and his coworkers[2,3] enabled us to identify the carbide phase. Several articles appeared after the present experimental work had been completed. Lucas and Wintrup[4] determined the solubility of carbon in molten iron-chromium-silicon alloys. Tofaute and his coworkers[5,6] have made detailed studies of the iron-chromium-carbon system, which will be referred to later.

Materials and Methods

Materials.—The iron, chromium and silicon used were essentially the same as those used in the investigation of the ternary system.[1] The

carbon was either sugar charcoal or "purified graphite." The manganese was a commercial variety of "carbon-free" material, which probably contained a small amount of aluminum. The electrolytic nickel contained a small amount of aluminum. The electrolytic nickel contained 0.013 per cent Fe, 0.11 per cent Co, and traces of Si. The concentrations of carbon, manganese and nickel in the quaternary alloys were so low that minor impurities in these materials are of no consequence.

Melting.—The alloys were made by several different methods. Small 1.5-gram melts were made by combining weighed amounts of analyzed ternary alloys and sugar charcoal in evacuated and sealed quartz tubes. These tubes were heated in an oxygen-gas flame and the melts were thoroughly agitated. Probably a small amount of silicon was taken up by reaction between the metal and the quartz, but the tubes showed very little evidence of chemical action on the inside. The small size of these ingots precluded analysis. Seven alloys were made in this way (Table 1).

TABLE 1.—*Phases Observed in 0.11 Per Cent Carbon Alloys*

Alloy No.[a]	Cr, Per Cent	Si, Per Cent	Temperature, Deg. C.	Phases[b]
13-C.....................	14.86	6.51	800	$a + c$
18-C.....................	12.28	12.82	800	$a + c$
34-C.....................	16.50	2.97	800	$a + c$
31-C.....................	16.86	9.11	800	$a + c + \Sigma$
31-C.....................	16.86	9.11	1000	$a + c$
33-C.....................	29.38	5.42	800	$a + c + \Sigma$
33-C.....................	29.38	5.42	1000	$a + c$

[a] The number indicates the original ternary alloy; the "C" that carbon has been added.

[b] Measurements of the lattice parameters showed that the presence of 0.11 per cent C lowered the values by about 0.0005Å. unit. This change is so small that it is entirely within the experimental error. The Σ-phase was identified from X-ray lines; the carbide phase by microscopic examination.

All the remaining alloys were made by mixing weighed quantities of the materials, frequently in the form of master alloys and high-carbon cast irons, in Norton alundum crucibles, and melting in vacuo by means of high-frequency induction heating. The master alloys, weighing from 400 to 500 grams, were also made in this way. All analyses of these alloys were reported to us by Mr. C. O. Burgess of the Union Carbide and Carbon Research Laboratories. There are three series of alloys, M-I, M-II and M-III indicating the "master alloy" used. The carbon containing alloys of the M-I series were made by melting the master alloy with carbon in weighed amounts. The carbon losses were so erratic that for the M-II and M-III series, cast irons were made by melting the

respective master alloys with excess of graphite. M-II cast iron contained 4.10 per cent C; M-III cast iron, 3.54 per cent C. Microscopic examination showed that both samples contain free graphite. In all tests the alloys were allowed to cool nearly to room temperature in the vacuum tube before the vacuum was broken and the alloy removed. This generally required about half an hour. Alloys in this condition are referred to as "as cast" in this report.

Heat-treatment.—Part of each alloy was heated in a hydrogen atmosphere for one week at approximately 1000° C., to eliminate any coring or lack of chemical homogeneity, and then furnace-cooled. This furnace-cooled from 1000° to 600° in about 2 hr. In some special cases, alloys in massive form were quenched from definite temperatures and the hardness was determined. After homogenizing, the alloys were ground in a mortar or with an alundum wheel to secure the finely divided material necessary for the powder methods of X-ray analysis. Each powder was sealed into an evacuated glass or quartz tube and annealed at a determined temperature in a vertical furnace, after which it was quenched by breaking the tube under water.[7] The time for chilling from furnace to room temperature is a small fraction of a second. The annealing temperature of the powder is the temperature cited in connection with the X-ray results.

X-ray Methods.—These are quite the same as those used for the work on the ternary system. The focusing cameras were of the Phragmén type, which divide the total range of reflections among three cameras. The large angle reflections are used for lattice-parameter measurements. The middle-range camera is particularly useful in phase-identification work with these alloys; the diffraction patterns of the several phases are distinctive in this range, and the characteristic reflections are sufficiently strong for comparatively small amounts of a phase to be discovered. However, lack of diffraction lines of a phase does not prove the absence of small amounts or traces of the phase. For example, the presence of a carbide phase has frequently been found by microscopic examination during the course of this work when the X-ray patterns gave no evidence of such a phase. Reference films were used to identify the alloy phases.

EXPERIMENTAL RESULTS

The results obtained in this investigation are summarized in Tables 1 to 6. Their interpretation in the light of the problems set for investigation follows in later sections. In columns headed "Phases," the following symbols are used:

a = alpha phase.

c = a carbide phase (see text for identification).

Σ = the phase that starts at the binary boundary in the neighborhood of the composition FeCr and extends into the ternary system.

This phase will be called the "sigma phase" in conformity with the earlier work.[1]

TABLE 2.—*Experimental Results on Series M-I Alloys*

Alloy No.	Composition, Per Cent				Anneal, Deg. C.	Phases		Lattice Constant
	Cr	Si	C	Mn or Ni		X-ray	Micro	
M-I.........	22.75	5.05	0.05		800	$a + \Sigma$		2.8577
			0.06		FC[a]		$a + \Sigma$	
M-I-2.......			0.18		997	a		2.8572
					595	$a + \Sigma$		2.8572
					FC		$a + \Sigma + c$	
M-I-4.......			0.39		1020	a		2.8568
					505	$a + \Sigma$		2.8564–2.8565
					FC		$a + c$	
					(Quench 700)		$a + \Sigma + c$	
M-I-3.......			0.63		1015	a		2.8554
					505	$a + \Sigma(?)$		2.8554
					FC		$a + c$	
M-I-21......	22.12	5.09	1.22		1000	$a + c$		2.8517–2.8520
			1.19		607	$a + c$		2.8520
					FC		$a + c$	
M-I-5.......			0.04	Ni	1000	a		2.8575
				0.49	600	$a + \Sigma$		2.8570
					FC		$a + \Sigma + c$	
M-I-6.......				1.96	1000	a		2.8583
					595	$a + \Sigma$		2.8579
					FC		$a + \Sigma + c$	
M-I-7.......			0.05	Mn	1000	a		2.8578
				0.11	803	$a + \Sigma$		2.8579
					640	$a + \Sigma$		2.8579
					FC		$a + \Sigma + c$	
M-I-8.......				1.16	1000	a		2.8577
					803	$a + \Sigma$		2.8579
					640	$a + \Sigma$		2.8581
					FC		$a + \Sigma + c$	
M-I-26 ...	22.01	4.95	0.05	1.76	975	a		2.8581
					593	$a + \Sigma$		2.8578
					FC		$a + c + \Sigma$	

[a] FC indicates furnace-cooled ingots (see text).

Effect of Carbon

The microscopic evidence shows that the solubility of carbon in these alloys is very small. Thus, in many of the alloys containing less than 0.06 per cent C, small polyhedra of carbides are observed. In all the small ingots containing 0.1 per cent added carbon, small, but appreciable

amounts of carbides were found. As the percentage of carbon is increased, the amounts of the carbides increase. In the slowly cooled

TABLE 3.—*Experimental Results on Series M-II Alloys*

Alloy No.	Composition, Per Cent				Anneal, Deg. C.	Phases		Lattice Constant
	Cr	Si	C	Mn or Ni		X-ray	Micro	
M-II.................	16.53	7.23			965	a		2.8510
M-IIb...............	17.15	7.22	0.025		604	$a + \Sigma$		2.8525–2.8522
(M-IIb as cast).......	17.18	7.40	0.014		600	$a + \Sigma$		2.8523
					FCª		$a + ?$	
M-II-16.............	16.84	7.34	0.30		950	$a + c$		2.8488
			0.31		570	$a + c$		
					FC		$a + c$	
M-II-15.............			0.51		950	$a + c$		2.8486
			0.55		570	$a + c$		
					FC		$a + c$	
M-II-13.............			0.98		1000	$a + c$		2.8455 (poor)
					600	$a + c$		2.8438 (poor)
					FC		$a + c$	
M-II-14.............	15.57	8.25	1.78		1000	$a + c$		2.8369 (poor)
			1.85		590	$a + c$		
					FC		$a + c$	
M-II-9.............			0.025	Ni	980	a		2.8505 (poor)
				0.50	815	$a + \Sigma$		2.8507
					580	$a + \Sigma$		2.8515
					FC		$a + \Sigma$ + c tr	
M-II-10.............				1.92	980	a		2.8507 (poor)
					815	$a + \Sigma$		2.8507
					580	$a + \Sigma$		2.8515 (very poor)
					FC		$a + \Sigma$ + c tr	
M-II-11.............				Mn	1000	a		2.8510
				0.38	598	$a + \Sigma$		
					FC		$a + c$ tr.	
M-II-12.............			0.05	1.40	1000	a		
					598	$a + \Sigma$		
					FC		a	
M-II-27.............	16.52	7.15	0.025	2.42	972	a		2.8513
					625	$a + \Sigma$		2.8524
					FC		$a + c$	
M-IIb-28.............	16.39	7.13	0.02	4.58	972	a		
					625	$a + \Sigma$		
					FC		$a + c$ + Σ tr.	

ª Furnace-cooled.

alloys, there is a tendency for the carbides to segregate around the grain boundaries. With still higher carbon percentages, the carbides occur in

elongated masses or plates.   Beyond 1 per cent C a substantial portion of the alloy is made up of the carbide phase.

The X-ray photograms do not show the presence of carbides when the amount of carbon is small, say up to approximately 0.3 per cent.   At 600° C. the presence of the sigma structure is clearly shown, but at

TABLE 4.—*Experimental Results on Series M-III Alloys*

Alloy No.	Composition, Per Cent				Anneal	Phases		Lattice Constant
	Cr	Si	C	Mn or Ni		X-ray	Micro	
M-III......	14.61	9.37	0.04		965°	a		2.8445 (poor)
					600	a + Σ		2.8410
					FC^a			
M-III-22...	14.68	9.34	0.28		960	a		2.8425 (very poor)
					612	a + Σ		2.8410
					FC		a + c + Σ(?)	
M-III-23...			0.66		940	a + c		2.8401
					612	a + c		2.8403
					FC		a + c	
M-III-24...			1.09		1000	a + c		2.8384
					600	a + c		2.8383
					FC		a + c	
M-III-25...	15.29	8.32	2.24		1000	a + c		2.8336
					612	a + c		2.8334
					FC		a + c	
M-III-17...	14.60	9.50	0.03	Ni 0.52	1000	a		2.8427 (poor)
					625	a + Σ		2.8411 (poor)
					FC		a + Σ	
M-III-18...			1.93		1000	a		2.8423 (poor)
					625	a + Σ		2.8413
					FC		a + Σ	
M-III-19...	14.61	9.37	0.04	Mn 0.39	961	a		
					610	a^b		2.8412
					FC		a + Σ	
M-III-20...				Mn 0.83	961	a		
					610	a + Σ		2.8414
					FC		a + Σ	

^a Furnace-cooled.
^b Not taken in best camera range for Σ-phase.

1000° C. only the alpha phase is indicated in these low-carbon alloys. When the carbon percentage exceeds 0.3 to 0.4 per cent the sigma phase could not be found by any means.   The amount of carbon that just causes the sigma phase to disappear apparently depends on the original matrix composition.

In the two cast irons, the phases observed under the microscope are alpha iron, carbide and graphite.   The exact point at which graphite

makes its appearance has not been ascertained. However, with 3.5 per cent C the amounts of graphite are considerable.

The lattice constant of the alpha phase as a function of the carbon content is plotted in Fig. 1. A sharp decrease in lattice constant is evident. Dashed vertical lines have been placed on each of the curves of the alloy series in order roughly to indicate the probable limit of the sigma phase. The changes in the slopes of these curves in the range
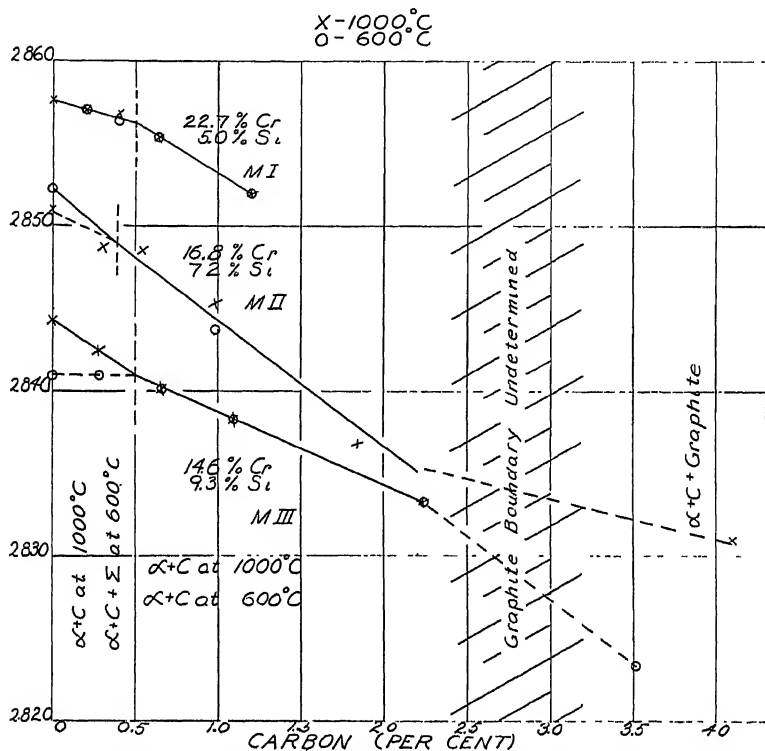
FIG. 1.—EFFECT OF CARBON ON LATTICE PARAMETERS AND PHASES PRESENT.

between 0.35 and 0.5 per cent are probably significant. At 600° C. the breaks in the curves coincide with the phase change: alpha + carbide + sigma to alpha + carbide, and this may in part be responsible for the breaks; but for the shape of the curves at 1000° C. no adequate interpretation has been found. It is also to be noted that when the carbon content exceeds these compositions, the temperature has no effect on the solubility of the carbides, and the alpha-phase composition is independent of annealing temperature. This statement applies only to the limited range covered in this investigation; i.e., 600° to 1000° C. To the left of these compositions, a region is indicated in which the alloys of the M-II and M-III series clearly show a change in the iron lattice parameters with temperature, and, therefore, in the matrix composition.

However, since a temperature change here causes change in the amount of a sigma phase, it cannot be decided from these parameter measure-

TABLE 5.—*Comparison of Sin² θ Values of Trigonal and Cubic Chromium Carbides with Carbides in Present Alloys*

SIN² θ VALUES AND INTENSITIES CR-KA RADIATION

Residues and Cast Iron		Trigonal Carbide		Cubic Carbide		Trigonal Carbide with 55 Per Cent Fe
				S	0.231	
W	0.254	S	0.250			0.254
				S	0.277	
		W	0.281			
W	0.296	S	0.291			0.296
		W	0.306			
M	0.319	S	0.314	S	0.311	0.319
		W	0.321			
		M	0.339			
		W	0.362			
				M	0.370	
VVW	0.390	M	0.384			0.391
S	0.405	S	0.397	S	0.404	0.405
VVW	0.417	W	0.412	M	0.416	0.419
W	0.434	M	0.428			0.435
VW	0.450	W	0.447			0.455
Lattice constants....		$a = 13.98$ $c = 4.523$		$a = 10.638$		$a = 13.86$ $c = 4.49$

TABLE 6.—*Effect of Carbide Composition on Temperature at Which Precipitation of the Sigma Phase Should Begin*

Alloy No.	Wt, Per Cent			Precipitation Temperature of Sigma Phase if Carbide Is		Phases Observed	
	Cr	Si	C	Cr_7C_3	$Cr_3Fe_4C_3$	X-ray	Micro[a]
M-I-4.........	22.75	5.05	0.39	810° C	900	$a + \Sigma(505°)$	$a + \Sigma + c$[d]
M-I-3.........	22.75	5.05	0.63	690	900	$a + \Sigma(?)(505°)$[c]	$a + c$
M-II-16.......	16.84	7.34	0.31	780	900	$a + c(570)$	$a + c$
M-II-15.......	16.84	7.34	0.53	580[b]	900	$a + c(570)$	$a + c$
M-III-22.......	14.68	9.34	0.28	640	850	$a + \Sigma(612)$	$a + c + \Sigma(?)$
M-III-23.......	14.68	9.34	0.66	200[b]	720	$a + c(612)$	$a + c$

[a] One week at 1000° C. Furnace-cooled from 1000° to 600° C. in about 2 hr. and then to room temperature in the same furnace.

[b] Outside range of curves and therefore doubtful.

[c] Annealing time probably too short at this low temperature.

[d] One week at 700° C. and furnace-cooled.

ments alone whether temperature has any effect on the solubility of the carbides.

There are at least four carbides in the iron-chromium-carbon system, each of which may contain both iron and chromium within certain limiting ranges of composition. The question of which carbide occurs here was answered by means of the following experiments: Large portions of alloy M-I-4, and the cast irons of M-II and M-III were treated with dilute hydrochloric acid and the residues carefully dried. To investigate the carbide phase at low carbon content, a special alloy weighing about 100 grams was made, containing approximately 23 per cent Cr, 5 per cent Si, and 0.18 per cent C. The inclusions were extracted by dissolving the matrix in dilute hydrochloric acid. The films from cast irons powdered in the usual fashion, and also from the residues, were compared with the results of Westgren, Phragmén and Negresco.[2,3] These investigators found three chromium carbides, each of which dissolved a considerable amount of iron. Only two concern us here. The first is cubic and the more recent work of Westgren has shown it to be based on a compound $Cr_{23}C_6$. It may contain as much as 35 per cent Fe by replacement of the chromium. This carbide has been found when the gross ratio of percentage of chromium to percentage of iron in an alloy lies approximately between 0.4 and 3.1; the upper (high-chromium) limit is less certain than the lower, and there are overlapping fields in certain ranges of Cr:Fe ratios, in which the cubic and the trigonal carbide, described below, are found present simultaneously.

The second carbide is of trigonal symmetry, and is based on the compound Cr_7C_3. It may contain as much as 55 per cent Fe. In alloys with carbon contents ranging from 2 to 4 per cent, this carbide has been found when the gross Cr:Fe ratios are between approximately 0.15 and 0.42. All three of our master alloys are within this range. The work of Westgren et al. also indicates that at constant carbon content increasing ratios of Cr:Fe in the gross alloy compositions give increasing Cr:Fe ratios in the trigonal carbide. This holds also for the cubic carbide. The presence of silicon will modify these relationships of course (see later). The third chromium carbide, Cr_3C_2 (rhombic), is entirely outside the range of composition of the alloys investigated. The fourth carbide is cementite, which can also dissolve a certain amount of chromium, but we have found no evidence of this phase in any of our alloys.

The photograms from the hydrochloric acid residues of alloy M-I-4, the special low-carbon alloy, and the cast irons of series M-II and M-III gave line systems of identical patterns, but showing small displacements of the lines, and differing in the relative intensities of the lines of the alpha and carbide phases. The close relationship between the lines found on these films and those found by Westgren et al.[2,3] for the trigonal carbide is shown in Table 5. For comparison, the lines from the cubic phase are included. The $\sin^2 \theta$ values observed are all somewhat larger than for the pure trigonal chromium carbide, indicating a slightly smaller

lattice; this in turn indicates that the carbides in these alloys contain a certain amount of iron. The last column of the table gives the values of $\sin^2 \theta$ for a carbide containing 55 per cent Fe, which, according to Westgren, Phragmén and Negresco, should have the lattice constants $a = 13.86$ and $c = 4.49$Å. The cast irons from which these carbide lines were secured contained respectively 3.54 and 4.10 per cent C, part of which was in the form of graphite. The agreement between the observed results and those calculated on this basis is excellent, but, because of the
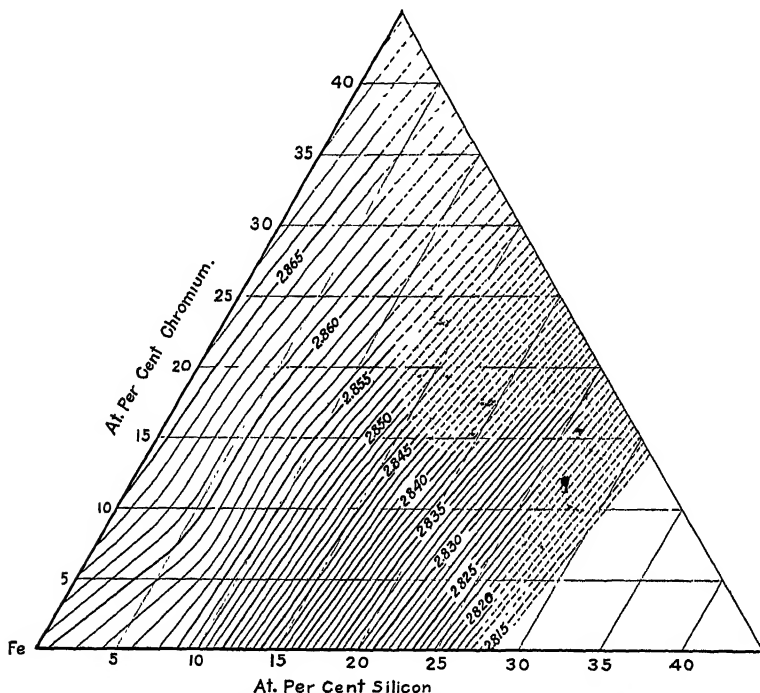
Fig. 2.—Parametric surface; isoparametric curves in alpha solid solution region; room temperature; atomic per cent. (From Andersen and Jette:[1] *Trans.* Amer. Soc. Metals, June, 1936, 392.)

relatively low accuracy of the $\sin^2 \theta$ values in the range covered in Table 6, this must not be considered as conclusive evidence that the carbide has 55 per cent Fe. In view of one of the conclusions that will be drawn later, it should be emphasized that as the carbon content increases chromium is rapidly removed from the matrix by the carbon in these alloys, and the alpha-phase composition and its Cr:Fe ratio becomes progressively different from the gross alloy composition and Cr:Fe ratio. As the carbide removes chromium and iron, the concentration of silicon in the matrix increases, and this in itself would cause the diminution of the lattice constant (Fig. 2). The carbide existing under these conditions is quite different in composition from that in a low-carbon alloy,

although in the alloys included in the present investigation it is still the trigonal carbide. Closer determination of the iron contents of the carbide phase from the lower carbon alloys was not possible because of the faintness of reflections at high angles; such reflections must be available for accurate determinations of lattice constants, and in many cases they did not occur on the films. The amounts of alloys available were in
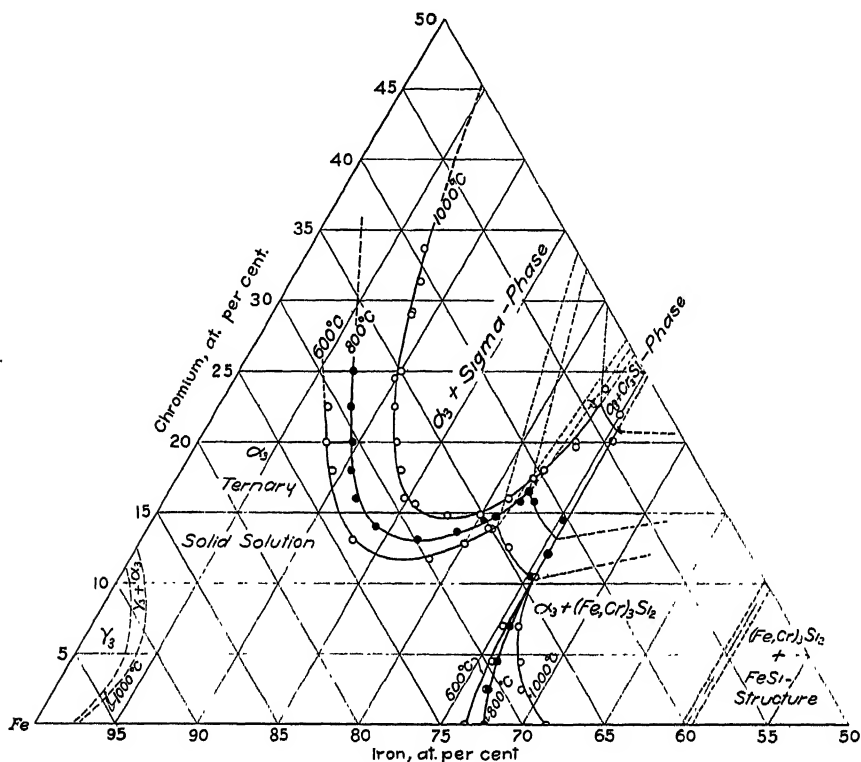
FIG. 3.—CONSTITUTIONAL DIAGRAM OF IRON-RICH SOLID SOLUTION RANGE. ATOMIC PER CENT. (From Andersen and Jette:[1] *Trans.* Amer. Soc. Metals, June, 1936, 404.)

general insufficient for making hydrochloric acid extractions and work with the residues. We may, however, accept without reservation that the carbide separating from the alloy at carbon contents at and above approximately 0.25 per cent is the trigonal chromium carbide with the basic formula Cr_7C_3, but containing more or less iron, depending upon the composition of the alloy.

The X-ray results were used in an indirect way to determine the composition of the trigonal carbide. From Tables 2, 3 and 4, it will be noticed that at all temperatures below 1000° C. the sigma phase disappears between 0.3 and 0.6 per cent C. Taking compositions in the critical range (e.g., M-I-4) corresponding to the range in which sigma

and alpha may coexist in the ternary system, it was assumed that all the carbon was in the form of the trigonal carbide, first as pure Cr_7C_3, and second, that the carbide contained 55 per cent Fe by weight. The latter composition corresponds nearly to the formula $Cr_3Fe_4C_3$. In this way, two new alpha-phase compositions were calculated for each alloy. These compositions were then plotted on the triangular diagram of the parametric surface of the iron-chromium-silicon system (Fig. 2). From these points the corresponding lattice parameters could be read. If for any one alloy the two calculated compositions of the matrix are connected by a straight line, and the actual alpha-phase composition lies between these limits, the isoparametric curve (Fig. 2) corresponding to the measured lattice parameter should cut the straight line. In four of the six cases it does so. In the other two, it misses the limit corresponding to the carbide Cr_7C_3 by an amount that is within the experimental error. Alloy M-II-16 shows the larger deviation. Because of the small angle between the line connecting the two compositions and the equiparametric curves, the results are not very conclusive regarding the composition of the carbide. At most this treatment gives a rough indication that the carbide is probably closer to Cr_7C_3 than to $Cr_3Fe_4C_3$. This indicates that on constant silicon isotherms in the quaternary systems the stability field of the trigonal carbide and alpha phase is widened out towards the chromium direction.

The alpha-phase compositions calculated above were then plotted on the equilibrium diagram (Fig. 3), and by interpolation or extrapolation the temperature at which the sigma phase should begin to precipitate was estimated. These results are given in Table 6. For convenience, the phases observed at different temperatures noted in Tables 2, 3 and 4 are given in the last two columns. All of the original carbon-free master alloys would begin to precipitate the sigma phase at about 950° C.

All these results, except those from alloy M-II-16, are consistent with the assumption that the carbide phase is high in chromium and approaches the composition of Cr_7C_3. The exception is an alloy that has given inconsistent results, as already noted.

A study of the present results in the light of the diagrams given by Tofaute, Küttner and Büttinghaus[6] indicates that silicon in the range between 5 and 9.3 per cent narrows, with respect to both chromium and carbon, the two-phase region alpha + $(Fe,Cr)_{23}C_6$, and the three-phase region alpha + $(Fe,Cr)_{23}C_6$ + sigma. Silicon increases the ranges of alpha + $(Fe,Cr)_7C_3$ and alpha + $(Fe,Cr)_7C_3$ + sigma. The cubic carbide $(Fe,Cr)_{23}C_6$ was not found in any of these alloys.

The graphitizing effect of silicon is also apparent; in no case was evidence of cementite [in this case $(Fe,Cr)_3C$] found by X-ray tests. The complexity of the phase relationships in the solid state in these alloys preclude a comparison with the results of Lucas and Wintrup.[4]

However, by reference to Fig. 1 and to the ternary diagrams in reference 6, it may be seen that silicon, which easily graphitizes cementite, has no comparable effect on the chromium carbides. Thus, contrary to cementite, chromium carbides should be expected to be quite stable in high-silicon cast irons.

The effect of silicon on the stability range of the gamma-iron phase, whether alone or in equilibrium with other phases, cannot be estimated from the available results because of the well-known fact that this phase can be retained by quenching only in exceptional cases.

We may safely draw the following conclusions regarding the effect of carbon in these alloys:

1. The solubility of carbon in the alpha phase is very low and probably in the vicinity of 0.02 to 0.04 per cent.

2. The effect of larger carbon contents is to diminish the lattice parameter of the alpha phase, the plot of a_0 vs. per cent C showing a discontinuity between 0.35 and 0.5 per cent C., depending upon the gross alloy composition.

3. For carbon contents greater than the point of discontinuity, the carbide phase has trigonal symmetry and is based on a compound of the formula Cr_7C_3.

4. The carbide contains some iron, but more chromium than iron is removed from the alpha phase. At carbon contents higher than the break in the curve the composition of the alpha phase is independent of annealing temperature.

5. It is easily possible to change the composition of the alpha-phase matrix by the addition of carbon to the point where it will remain as alpha phase at all temperatures. The carbon content at which the precipitation of the sigma phase becomes impossible apparently coincides with the break in the curve (Fig. 1).

6. The obvious manner to correct for the presence of carbon is to use 10 units by weight of additional chromium for each unit of carbon present.

7. No evidence of gamma-iron formation from either X-ray or microscopic examination has been found in the carbon containing alloys.

Effect of Nickel and Manganese

The effects of added nickel and manganese on the lattice parameters are small. The lattice parameters of the alpha phases remain constant within experimental error even up to the highest concentrations studied, 2.0 per cent Ni and 4.6 per cent Mn. No appreciable effect on the positions of the sigma-phase lines could be observed. In part, this lack of appreciable influence on the lattice constants is due to the close similarity of atomic sizes of iron, chromium, nickel and manganese. Neuberger[8] gives for the radii of these elements, respectively, 1.239, 1.247, 1.243 and

1.247Å. A second factor is the comparatively low concentration used. The close similarity in atomic sizes, however, would permit fairly extensive substitution of nickel or manganese for iron and chromium, not only in the alpha phase but also in the sigma phase, and probably in the carbides.

The precipitation of the sigma phase seemed not to be markedly affected. Any change in the solubility surface of the alpha phase would be extremely difficult to detect, and in these concentrations it is probably negligible for practical purposes. In the alloys slowly cooled after annealing at 1000°, all specimens examined showed that the sigma phase tends to segregate at the grain boundaries.

In the M-I and M-II series the amount of sigma phase seen under the microscope in the slowly cooled alloys appears perhaps somewhat greater in alloys with lower nickel content. In the M-III series there is little difference in this respect between the 0.5 and 2.0 per cent Ni alloys. In the manganese alloys of series M-I and M-II, the amount of sigma phase seems to be practically independent of the amount of manganese. Alloys having high manganese content nearly always showed coring and segregation. High manganese appears also to diminish the tendency to large grain size, which is so obvious in most of the carbon-free alloys.

Since both nickel and manganese are "austenite formers," or "gamma formers," in iron alloys, there was a possibility that a gamma-phase region would be found in these alloys. When the gamma phase occurs in sufficient amount in the specimen exposed to the X-rays, its characteristic pattern will be found on the film, of course. If, however, the gamma phase is stable only at high temperatures, and cannot be retained by a quenching operation, the alpha lines are generally badly blurred. This is due to the difference in equilibrium concentrations in the alpha and gamma solid solutions and lack of time to reach the low-temperature equilibrium. However, even with the highest concentration of nickel and manganese used, no evidence for the existence of a gamma phase was found by these criteria in the alloys, nor could any austenite be detected by microscopic methods applied to the slowly cooled alloys.

The conclusions that may be drawn from the present results are:

1. The effect of nickel and manganese on the lattice parameters of both alpha and sigma phases is practically negligible in these concentrations.

2. In the present investigation we were unable to detect with certainty any effect on the solubility surface of the alpha phase.

3. There was no observable tendency to form a gamma-iron phase. There are evidently sufficiently high concentrations of the two "alpha formers," chromium and silicon, to counteract any tendency in this direction. If it is desirable to add either of the elements nickel or manganese within the limits covered by the present investigation, to improve other properties, it can safely be done.

ACKNOWLEDGMENT

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DISCUSSION

Notes on Microstructure and Hardness of Alloys Consisting Essentially of Iron, Chromium and Silicon

By A. G. H. Andersen* and Eric R. Jette,† Members A.I.M.E.

A few years ago, while the writers worked on the constitution of ternary and quaternary alloys consisting mainly of iron, chromium and silicon[1,2] some information on microstructures and hardness, not incorporated in the published work, was obtained. It has not been possible to do any further work on the properties of the alloys. The information possessed is hereby presented for the interest it may have in connection with the constitution of the alloys.

Microstructures

Referring to the iron-chromium-silicon diagram,[1] the regions that received most attention were those in which the sigma phase appears. It was found that the mode of occurrence of this phase varied much with the condition under which it was formed, and the mode influenced considerably the hardness of the alloys. In some slowly cooled alloys, well within the alpha + sigma-phase boundary, sigma occurs in patterns suggesting a eutectic. The structure of such an alloy is shown in Fig. 1, showing it to be partly coarsely laminated and partly globular mottled. In other annealed and slowly cooled alloys, the laminated structure is entirely absent, and sigma appears in an irregular distribution of sharply cornered elongated areas (Figs. 2 and 3). These areas all possess a more or less mottled structure. A carbide phase is also visible in these two photomicrographs; it is represented by bright white areas of various shapes, sometimes apparently enveloping the sigma.

Quenched and aged specimens, whose compositions are located near the phase boundary between alpha and sigma + alpha regions, have structures not unlike martensite (Figs. 5 and 6). Fig. 4 shows the structure of alloy No. 35 as quenched from 1100° C.; it is a typical solid solu-

tion structure. Fig. 5 shows the same alloy aged at 610° C., while Fig. 6 shows the structure after a final aging at 830° C. Note that the structure has become coarser with the higher aging temperature.

FIG. 1.—ALLOY No. 13.   × 500.
    Cr, 14.86 per cent; Si, 6.51; C, <0.02. Annealed. Alpha plus sigma. Etch, HCl.
FIG. 2.—ALLOY M-I-2.   × 200.
    Cr, 22.75 per cent; Si, 5.05; C, 0.18. Annealed. Alpha plus sigma plus carbide. Etch,   HCl + FeCl₃.
FIG. 3.—ALLOY M-I-2.   × 1000.
    Composition same as Fig. 2. Etch,   HCl + FeCl₃.
FIG. 4.—ALLOY No. 35.   × 100.
    Cr, 28.14 per cent; Si, 5.11; C, 0.011. Quenched from 1100° C. Alpha iron. Brinell hardness 227. Etch,   HCl.

Study of many of these alloys seems to be complicated by the influence of the composition of the ternary alloys, as well as of additions of nickel, manganese and carbon on the etching characteristics.

Alloys consisting essentially of the sigma phase are hard to etch. Deeply etched electrolytically with ferrous sulphate-sulphuric acid solu-

tion, a distinctive corrugated structure with rarely any indications of grain boundaries is obtained. Occasionally the corrugations form a distinct rectangular Widmanstätten structure. Alloy No. 42, represented by Figs. 7 and 8, shows this structure.

It was also noted that alloys high in chromium often showed characteristic "skeleton" structures, generally gray. It is doubtful whether this constituent is sigma. Alloy No. 72, represented by Figs. 9 and 10, shows the "skeleton" constituent. Occasionally globular mottled, dark constituents are noted. Some of these are mottled. Similar inclusions
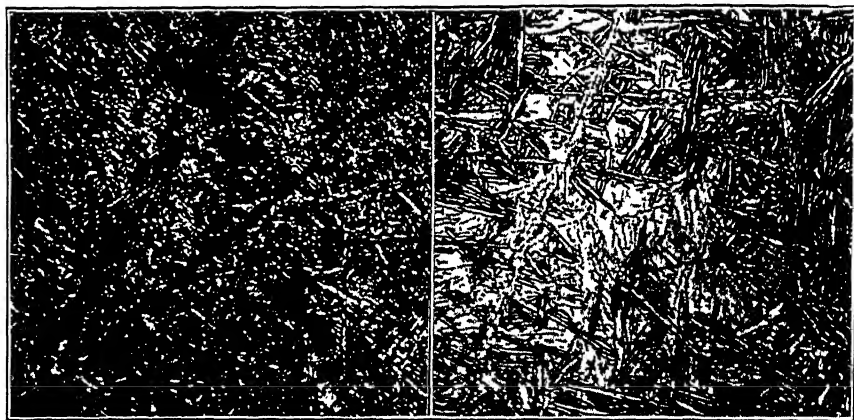
FIG. 5.   FIG. 6.

FIG. 5.—ALLOY No. 35. × 250.

Quenched from 1100° C. and aged at 610° C.   Martensitic structure, alpha plus sigma. Brinell hardness 520. Etch, HCl.

FIG. 6.—ALLOY No. 35. × 250.

Quenched from 1100° C. and aged at 710° C., reheated and held at 820° C. for 3 hr. Final Brinell hardness 472. Etch, HCl.

in high-chromium alloys have been seen frequently by others, and supposed to be iron chromites. Determination of the composition of these interesting inclusions is yet to be made. In polarized light with Nicols crossed other inclusions, which undoubtedly are glassy silicates, may be seen. They are distinguished from some of the globular constituent only by their appearance in polarized light.

The beta structure, very distinctly unlike the sigma, is shown in Fig. 11, which represents alloy No. 19.

It should, perhaps, be noted that in the two previous papers on the iron-chromium-silicon alloys[1,2] we first observed the sigma phase in the ternary alloys. Comparison of our X-ray photograms with one given by Wever and Jellinghaus identified it as a phase similar in structure to a phase they found in the binary, Fe-Cr system.[7] A similar photogram was given for an alloy of iron, nickel and chromium in another article, which appeared a little earlier.[8] This same phase had, however, been observed

earlier by Bain and Griffiths[5] in their work on the iron-nickel-chromium system and was called by them the "B" or "brittle" phase. This constituent was found in alloys containing about 0.2 per cent C and as little as 0.3 per cent Ni. They also described its more important properties.

FIG. 7.—ALLOY No. 42.   × 200.
Cr, 44.76 per cent; Si, 7.58; C, <0.02. As cast. Sigma phase. Electrolytic etch in H_2SO_4 and $FeSO_4$.

FIG. 8.—SAME SPECIMEN AS IN FIG. 7.   × 1000.

FIG. 9.—ALLOY No. 72.   × 200.
Cr, 34.21 per cent; Si, 1.21. Annealed. "Skeleton" constituent in alpha iron. Etch,   HCl + $FeCl_3$.

FIG. 10.—SAME SPOT IN SAME SPECIMEN AS FIG. 9.   × 1000.

There can be no doubt that in both ternary systems we have to do with an iron-chromium compound with a composition in the neighborhood of FeCr, which is capable of dissolving not only excess iron and chromium but also silicon and nickel. It may be of some interest to mention that Wever and Jellinghaus found this same structure in the iron-vanadium system.[9]

TABLE 1.—*Brinell Hardness Numbers of Iron-chromium-silicon Alloys*

Alloy No.	Composition, Per Cent		Hardness Numbers	
	Cr	Si	Annealed	Quenched
1	2.28	0.05	65	
2	4.42	0.05	93	
3	6.61		107	
4	8.79		110	
5	11.81	0.02	116	
6	1.01	0.48	95	
7	1.74	0.32	140	
8	2.54	1.34	169	
9	3.58	1.89	162	
11	8.36	4.67	215	
13	14.86	6.51	276	195
14	15.83	7.96	372	205
15	19.09	10.80	509	350
16	15.28	15.20	534	
17	20.16	10.37	495	
18	12.28	12.82	509	
21	2.64	16.16	496	
26	5.15	18.97	404	
27	3.15	26.53	465	
28	3.72	13.92	495	
29	1.09	15.63	484	
30	21.76	13.15	522	
31	16.86	9.11	379	
33	29.38	5.42	496	222
34	16.50	2.97	189	176
35	28.14	5.11	228	227
37	20.67	11.00	412	
38	23.93	4.43	230	213
39	8.38	8.90	342	
40	15.58	16.20	522	
41	16.63	17.77	515	
45	4.42	17.73	522	
46	7.40	16.07	513	
47	2.45	9.33	385	
49	32.19	4.46	358	222
50	22.90	6.28	263	232
51	6.64	6.58	338	
53	11.71	15.85	522	
54	35.70	15.30	532	
71	48.52	0.08	255	245
72	34.21	1.21	180	175
73	39.44	1.51	245	210
75	46.76	1.81		245
76	57.28	1.51	290	270

Bain and Griffiths presented photomicrographs which show the B (or sigma) constituent present in both austenite and ferrite matrices respectively, in alloys containing about 0.2 per cent C. Jette and Foote[6] later investigated the compound in the binary system.

HARDNESS TESTS

All hardness numbers were obtained originally on a Rockwell hardness tester and later converted to Brinell numbers by means of standard conversion tables. These values are given in Table 1.

The hardness varies considerably in the individual test pieces, particularly in the as-cast condition, therefore average values of at least three Rockwell numbers were used. If the first three values varied considerably, two or more additional readings were made. The quenched specimens from No. 71 upwards were quenched in 10 per cent brine at 35° C., after being held for 18 hr. at approximately 1025° C. All other quenched specimens were similarly treated except that the quenching temperature was 1100° C.

For hardness numbers of iron-chromium alloys and iron-silicon alloys see references 3 and 4, respectively.

AGING TESTS

A number of alloys whose compositions are close to the alpha-phase boundary were aged at various temperatures after having been quenched from 1025° or 1100° C. With an aging temperature of 700° C. as much as 100 per cent increase in hardness was obtained on some of the specimens. Microscopical investigation of the age-hardened specimens showed a martensitelike structure (Figs. 5 and 6). It is believed that this structure is caused by the precipitation of sigma in finely divided form; no verification by means of X-rays was made of this. It is recognized that the "precipitated" sigma may be a structurally more or less modified form of the equilibrium phase, giving slightly different X-ray reflections.

FIG. 11.—ALLOY No. 19. × 100. Cr, 7.93 per cent; Si, 16.83. Annealed. Alpha plus beta (Fe, Cr)$_3$ Si$_2$. Etch, HCl.

Table 2 gives the result of the aging tests. No attempt has been made to fix the optimum aging temperature and time.
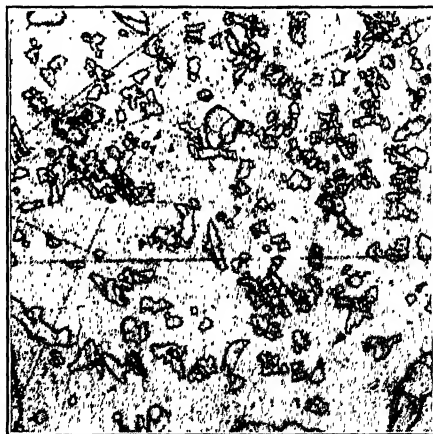
Table 2 shows that some of the alloys, while comparatively soft as quenched, become hardened by simple annealing. Others are soft in

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6	1.01	0.48	95	
7	1.74	0.32	140	
8	2.54	1.34	169	
9	3.58	1.89	162	
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40	15.58	16.20	522	
41	16.63	17.77	515	
45	4.42	17.73	522	
46	7.40	16.07	513	
47	2.45	9.33	385	
49	32.19	4.46	358	222
50	22.90	6.28	263	232
51	6.64	6.58	338	
53	11.71	15.85	522	
54	35.70	15.30	532	
71	48.52	0.08	255	245
72	34.21	1.21	180	175
73	39.44	1.51	245	210
75	46.76	1.81		245
76	57.28	1.51	290	270

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Cr, 7.93 per cent; Si, 16.83. Annealed. Alpha plus beta (Fe, Cr)₃ Si₂. Etch, HCl.

reflections. Table 2 gives the result of the aging tests. No attempt has been made to fix the optimum aging temperature and time.

Table 2 shows that some of the alloys, while comparatively soft as quenched, become hardened by simple annealing. Others are soft in

TABLE 2.—*Brinell Hardness Numbers*

Alloy No.	As Quenched	Aged at 700° C.						Annealed
		Hr.	No.	Hr.	No.	Hr.	No.	
13	195	12	290	24	280	48	290	276
14	205	12	242	24	242	Broke up		372
15	330	12	330	24	404	48	426	509
33	222	12	340	28	426	52	509	496
35	228	16	290	28	509	52	522	228
49	242	16	242	28	290	52	522	352
50 (610° C.)	228	45	300	90	393	112	448	263

the annealed as well as the quenched condition and hard after quenching followed by aging. This would indicate a simple precipitation process upon aging, and that for some of the alloys no great loss in hardness occurs upon overaging of the martensitic structure and agglomeration of much of the sigma in distinctly segregated particles.

HARDNESS OF QUATERNARY ALLOYS

The hardness of a number of quaternary alloys in the as-cast and in the annealed conditions are given in Table 3. These alloys are the same as those used for an X-ray examination previously reported.[2] They were made by adding small amounts of a fourth element to ternary master alloys of the following compositions:

	C_R	S_I	F_E
M-I	22.75	5.05	ball
M-II	16.53	7.23	ball
M-III	14.61	9.37	ball

It is seen that alloys containing manganese up to about 4 per cent and nickel up to 2 per cent show little variation in hardness, while carbon additions, as is to be expected, materially increase the hardness.

It may be said that experiments carried out by the Union Carbide and Carbon Research Laboratories show that alloys of higher chromium content that contain more than about 3 per cent Si are brittle, have low tensile strength and very small ductility. This is rather regrettable, since tests by the same laboratory show them to possess very good acid-resisting properties.

ACKNOWLEDGMENT

These experiments were carried out in conjunction with X-ray work on quaternary alloys,[2] in close cooperation with the Union Carbide and Carbon Research Laboratories. The chemical analysis of all the alloys in Table 3 were made by that laboratory. The writers hereby express

TABLE 3.—*Effect of Composition and Annealing on Hardness of Alloys Containing C, Ni or Mn*[a]

Alloy No.	Analysis, Per Cent	Brinell Hardness		Alloy No.	Analysis, Per Cent	Brinell Hardness		Alloy No.	Analysis, Per Cent	Brinell Hardness	
		As Cast	Annealed			As Cast	Annealed			As Cast	Annealed
M I-2	0.18 C		277	M II-16	0.31 C	325	350	M II-28	4.58 Mn	345	345
M I-4	0.40 C	250		M II-15	0.53 C	435	415	M III-22	0.28 C	450	415
M I-3	0.63 C		277	M II-13	0.98 C	490	425	M III-23	0.66 C	460	450
M I-21	1.21 C	450	425	M II-14	1.82 C	530		M III-24	1.09 C	515	490
								M III-25	2.24 C	565	540
M I-5	0.49 Ni		238	M II-9	0.50 Ni	320	320				
M I-6	1.96 Ni		238	M II-10	1.92 Ni	290	345	M III-17	0.52 Ni	380	380
								M III-18	1.93 Ni	390	375
M I-7	0.11 Mn		257	M II-11	0.38 Mn	330	325				
M I-8	1.16 Mn		277	M II-12	1.40 Mn	320	330	M III-19	0.39 Mn	380	380
M I-26	1.76 Mn	230	245	M II-27	2.42 Mn	345	325	M III-20	0.83 Mn	380	400

[a] The hardness of the original master alloys was not measured. The values are probably very close to those for corresponding low-nickel and low-manganese alloys.

their appreciation and thanks for the valuable aid of the officers and members of this organization.

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DISCUSSION

[This includes discussion of another paper by the same authors, beginning on page 303.]

(Oscar T. Marzke presiding)

O. T. MARZKE,* Worcester, Mass.—The first paper, in the opening paragraph, says: "Partly for the sake of theoretical interest, and partly because of the possible commercial importance of these alloys, the present investigation was undertaken." The last paragraph of the second paper mentions that certain of the alloys are rather brittle when the silicon exceeds 3 per cent, and says that this is rather regrettable since tests by the same laboratory show these alloys to possess very good acid-resisting properties. Is this property or the age-hardening capability the commercially important one?

A. G. H. ANDERSEN.—We did not wish to emphasize any particular possibility too strongly, but those two features were noticed and we took them both into account when we wrote "possible commercial importance." We wrote it so that those who would be interested in this type of alloys might find in the tests some starting point, rather than to imply that there was a certain promise of useful alloys.

O. T. MARZKE.—Was any work done to determine the high-temperature properties?

A. G. H. ANDERSEN.—No, we did not determine any high-temperature physical properties. These papers are essentially notes, which originally it was our intention to include in an earlier paper. However, at that time we thought it would be well to do some further research and then give out the results as a longer second paper. For various reasons, it was not possible to continue the research and so we wrote up these short notes for what they are worth.

O. T. MARZKE.—Are these alloys workable? I believe all of this information was obtained on the cast alloys. Is that correct?

A. G. H. ANDERSEN.—Yes, they were obtained on the cast alloys. We found it possible to work some of these alloys in 30-gram ingots. We have, however, not succeeded in cold-working any of them in ingots of larger sizes, or bars hot-rolled from such ingots. The Union Carbide and Carbon Co., after some initial difficulty, was able to hot-roll these alloys in ingot sizes of about 10 pounds.

* Research Laboratory, American Steel and Wire Co.

Grain Growth in Normalized Sheet Steel during Box Annealing

BY M. L. SAMUELS,* MEMBER A.I.M.E.

DURING the period from 1910 to 1920, there was a lively interest in the subject of grain growth and many papers were published, followed by interesting discussions. Questions dealing with the fundamentals of grain growth—why and how it occurs—were treated in papers by Howe,[1] Jeffries,[2] Sauveur,[3] Chappell,[4] Beilby,[5] Mathewson and Phillips,[6] McAdam,[7] Carpenter and Elam,[8] Stead and Carpenter,[9] Ruder,[10] as well as others.

Since that decade, much indeed has been done regarding the practical control of grain size, and it is now possible to order material having a size specified in the American Society for Testing Materials classification. Also, one hears the term "spliced boundaries" used in connection with certain tungsten lamp filaments[11] wherein it is important to prevent "sagging" between consecutive turns of the helix.[12]

This practical use of a certain knowledge as to the things that influence or even control grain growth should not be taken as an indication that the subject has been thoroughly explored and that nothing more can be learned from fundamental studies. It is with this thought in mind that a report of some observations and experiments on abnormal grain growth is believed justified. Abnormal grain growth is met with in heat-treating high-carbon steels in the austenitic range,[13] in the hardening treatments of high-speed steels,[14,15] and in the low-temperature annealing of strained low-carbon steels as in sheet and wire material. Entirely aside from these instances of exaggerated grain growth, which some might consider as freakish, it is thought that abnormal growth is simply a case where the growth forces and the forces tending to prevent growth are almost, but not quite, evenly balanced. Information relative to grain-growth characteristics in general may be obtained from a study of abnormal growth conditions, which may be looked upon as vantage points. Reflection will show at once that if growth forces are great in comparison to inertia or resistance to growth, many crystals start to grow and, for that reason, none becomes very large, whereas if inertia is

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[1] References are at the end of the paper.

predominant no growth at all takes place. Under conditions in which the forces are very nearly evenly balanced but with the urge to grow slightly predominating, a few widely scattered crystals may start growth at a time in the annealing cycle at which the vast majority of crystals less favorably situated are restrained and, therefore, the few favored crystals may feed upon the smaller neighbors and become abnormally large.

Abnormal growth of strained ferrite upon low-temperature annealing, first reported by Stead in 1898 and subsequently ascribed to a critical degree of strain by Sauveur, is a subject widely discussed in the papers mentioned above. Such straining has been considered a necessary prerequisite if abnormal growth was to take place during annealing, and it is for the purpose of reporting some instances of typical exaggerated growth without previous cold-working that this paper is written. Patience is asked of the reader to consider the experimental results that follow.

Experimental Results

Effect of Rate of Cooling from the Normalizing Temperature.—Fig. 1 shows a full cross section of hot-rolled $\frac{3}{16}$-in. strip after box annealing at 1450° F. The material is an ordinary rimmed sheet steel having the following composition: C, 0.07 per cent; Mn, 0.38; P, 0.012; S, 0.024.

The hot-rolled strip is finished at a dull red heat and the rate of heating and cooling in the upper part of the box-annealing cycle is approximately 10° F. per hour with about 3 hr. time allowed for soaking at maximum temperature. The marked abnormal growth on the surfaces here may, of course, be ascribed to "cold-work" during the finishing passes on the hot strip mill.

Fig. 2 is a specimen of the hot-rolled strip after holding 15 min. at 1850° F. and cooling in a tube furnace, the rate of cooling being about 40° F. per minute. Fig. 3 shows the material after cooling in the tube furnace, as in Fig. 2, and subsequently box-annealed at 1450° F. There has been but little change in grain size from this heat-treatment and one would say that the rolling strains present in the hot-rolled strip that caused the growth shown in Fig. 1 had been removed by the treatment at 1850° F.

Fig. 4 shows a specimen that was held 15 min. at 1850° F., cooled in the tube furnace (40° F. per minute), subsequently reheated to 1850° F. and held 5 min., after which it was pulled out into the air and then box-annealed at 1450° F. It is evident here that something happened during the normalizing from 1850° F., causing abnormal growth upon subsequent box annealing, which did not happen during the slightly slower cooling rate of 40° F. per minute. Compare Figs. 3 and 4.

This response was checked, of course, many times and identical results were always obtained.

Effect of Cooling Rates Slightly Slower than Those Produced by Normalizing.—An apparatus was made whereby the specimens could be withdrawn from the tube furnace so that cooling rates intermediate between true normalizing and furnace cooling (40° F. per minute) were obtained.
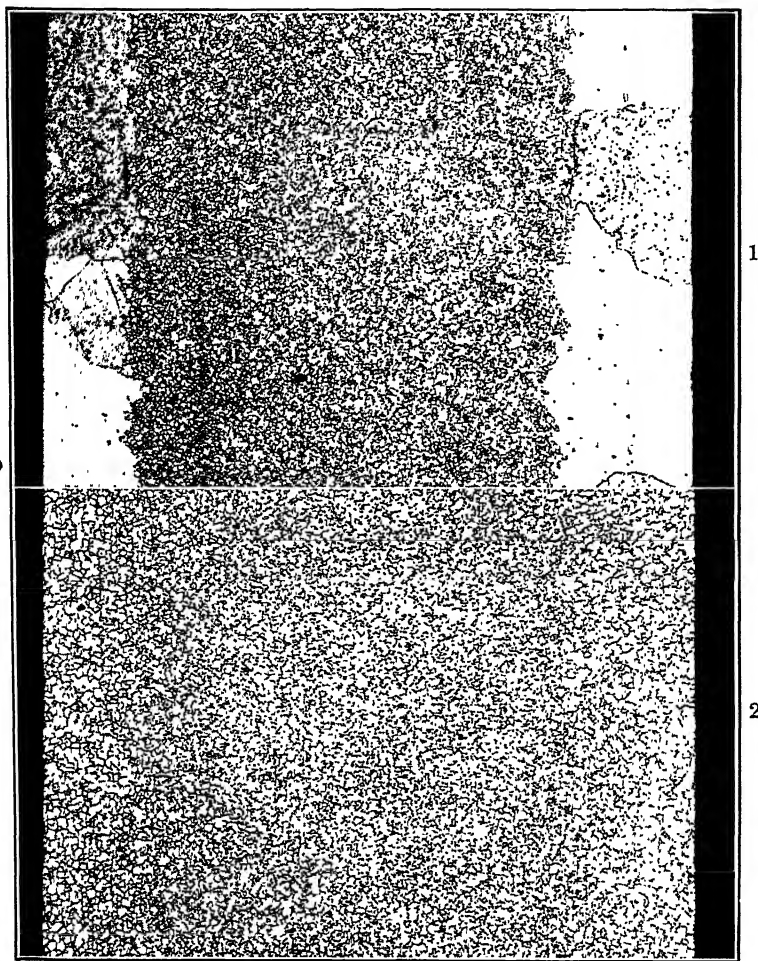
FIG. 1.—FULL CROSS SECTION OF $\frac{3}{16}$-INCH HOT-ROLLED STRIP BOX-ANNEALED AT 1450° F.

FIG. 2.—FULL CROSS SECTION OF $\frac{3}{16}$-INCH HOT-ROLLED STRIP HELD AT 1850° F. FIFTEEN MINUTES AND COOLED IN TUBE FURNACE 40° F. PER MINUTE. Both × 20. Specimens etched with nitric acid.

A counterweight attached to the specimen, by means of a wire that ran over pulleys, was allowed to float on mercury. The mercury could be let out through glass nozzles of assorted sizes so that the counterweight pulled the specimen up from the hot zone at rates determined by the size of the particular nozzle employed. A small thermocouple inserted in

specimens of identical size and shape as those later to be used in the tests was used to construct cooling curves for each nozzle size.

Specimens cooled from 1850° F. at rates intermediate between normalizing and cooling in the tube furnace also gave a graded series as regards
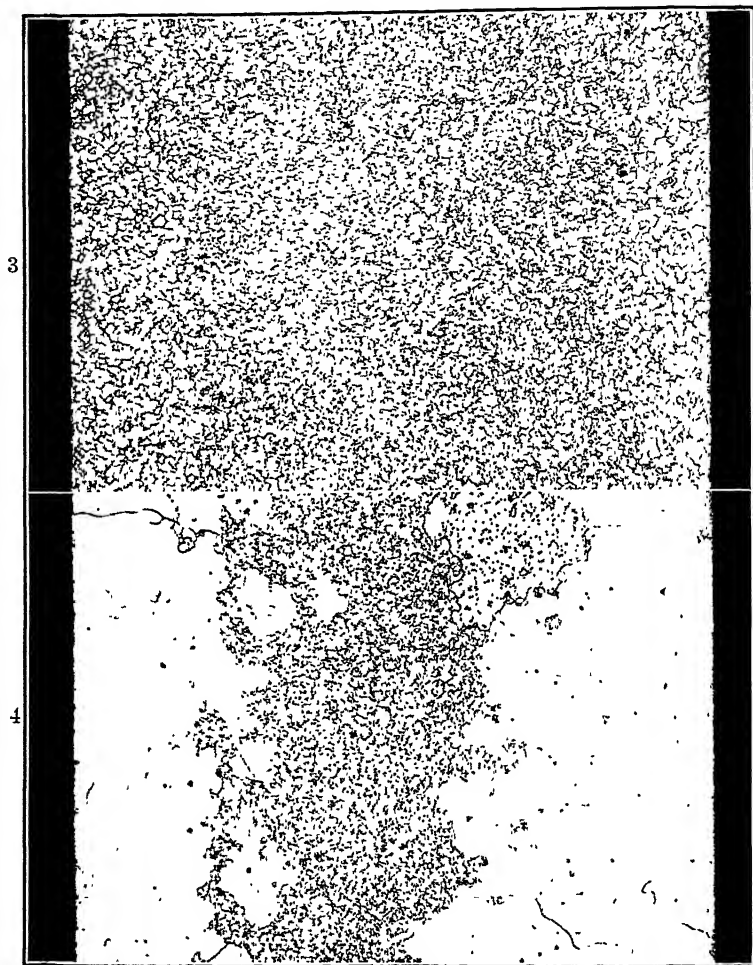
FIG. 3.—FULL CROSS SECTION OF $\frac{3}{16}$-INCH STRIP COOLED IN TUBE FURNACE (40° F. PER MINUTE) FROM 1850° F., BOX-ANNEALED AT 1450° F.
Note absence of abnormal growth.
FIG. 4.—FULL CROSS SECTION OF $\frac{3}{16}$-INCH STRIP COOLED IN TUBE FURNACE (40° F. PER MINUTE) FROM 1850° F., REHEATED TO 1850° F. AND COOLED IN AIR, BOX-ANNEALED AT 1450° F.
Both × 20.   Specimens etched with nitric acid.

grain growth upon subsequent box annealing at 1450° F., those cooled rapidly showing marked growth and those cooled less rapidly showing less growth.   The numerous photomicrographs showing this series are not included because of the excessive number of pictures involved.

Air Cooling and Quenching of Specimens from Points Ranging from Slightly above to Slightly below the Ar₃ Point.—It was thought that 'the speed of cooling through the critical range might be the controlling factor in the introduction of stimuli that cause excessive growth upon subsequent box annealing. Accordingly, the Ar₃ point for the particular steels being used and the tube-furnace rate of cooling was carefully determined as shown in Fig. 5. Specimens were heated to 1850° F., held 5 min. and then the furnace was shut off and allowed to cool. One specimen was removed and cooled in air after 5½ min. (Fig. 5): another specimen was treated in the same way but was allowed to cool 6 min. before removal from the furnace, and so on until an 8½-min. holding time was reached. This operation was repeated but this set of specimens was quenched in water instead of being allowed to cool in air.
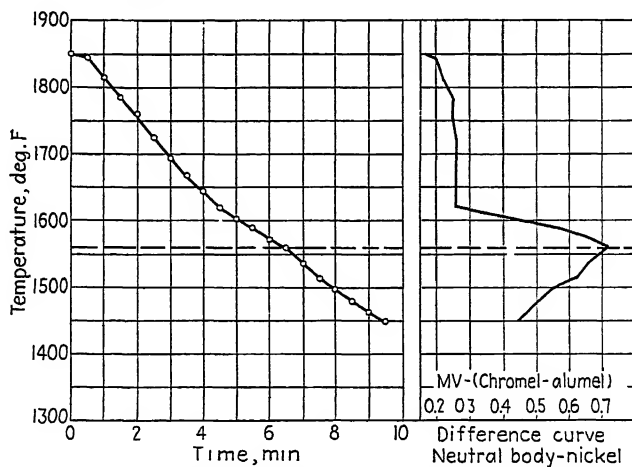
FIG. 5.—LOCATION OF AR₃ POINT WHEN COOLING RATE IS THAT AFFORDED BY TUBE FURNACE.

Subsequent box annealing at 1450° F. gave no growth in any of the air-cooled specimens, but the quenched group showed another graded series, growth being fairly well marked in the specimen quenched after only 5½-min. cooling time and playing out altogether after 7½ min. had elapsed. In none of these specimens was as much growth found as in the samples cooled in air from 1850° F. However, in this connection it should be remembered that the Ar₃ point is not truly a "point" but simply designates the temperature at which maximum separation of the alpha phase occurs. This fact can be seen clearly in the difference curve in Fig. 5.

Effect of Pre-box-annealing Heat-treatments upon the Physical Properties.—The steel used in this experiment was 20-gauge cold-reduced strip made for automobile fender stock of the following composition: C, 0.071 per cent; Mn, 0.37; P, 0.008; S, 0.022; Cu, 0.075.

Samples ¾ by 8 in. were cut adjacent to each other from the center of the 48-in. wide strip and duplicates were prepared. Three groups of samples were made up, each group containing specimens in the following four conditions:
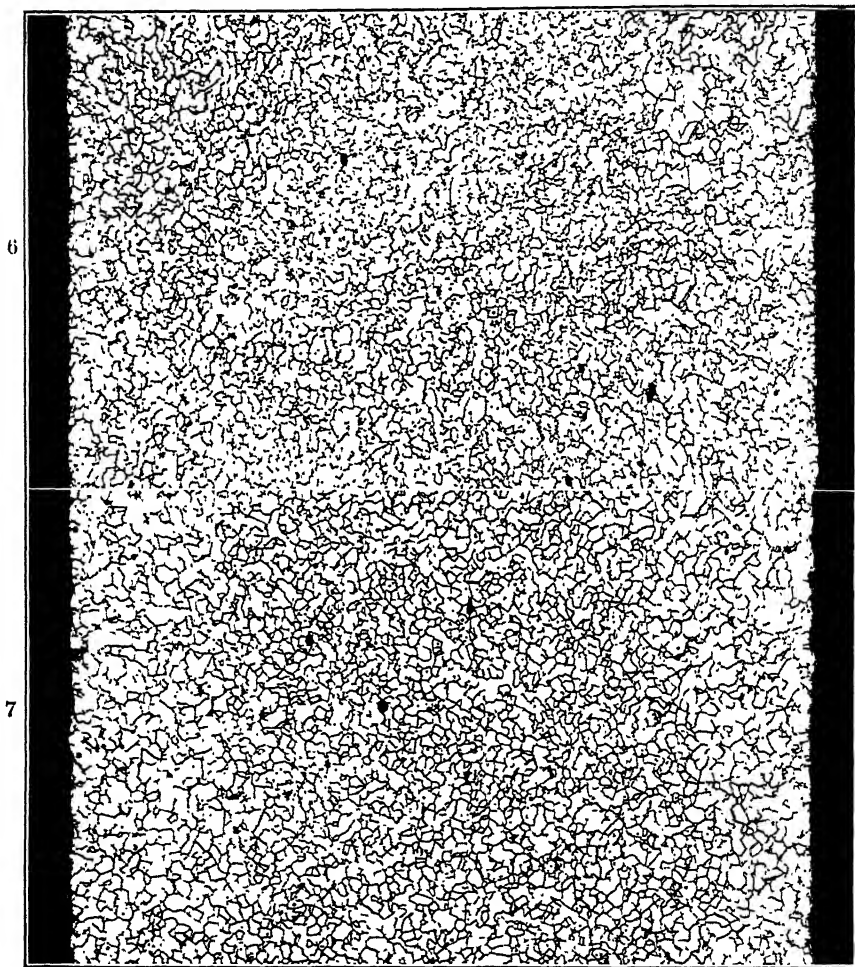
FIG. 6.—FULL CROSS SECTION OF COLD-REDUCED STRIP BOX-ANNEALED AT 1200° F. IN THE AS-RECEIVED CONDITION.
FIG. 7.—FULL CROSS SECTION OF COLD-REDUCED STRIP NORMALIZED AT 1850° F. AND BOX-ANNEALED AT 1200° F.
Both × 100. Specimens etched with nitric acid.

1. No treatment; cold-reduced material.
2. Normalized from 1850° F.
3. Cooled down in the tube furnace from 1850° F. (40° F. per minute).
4. Cooled in the tube furnace and subsequently normalized from 1850° F.

The three groups of specimens were then box-annealed under ordinary commercial conditions and the following range of box-annealing temperatures was obtained: group 1, 1200° F.; group 2, 1375° F.; group 3, 1450° F.
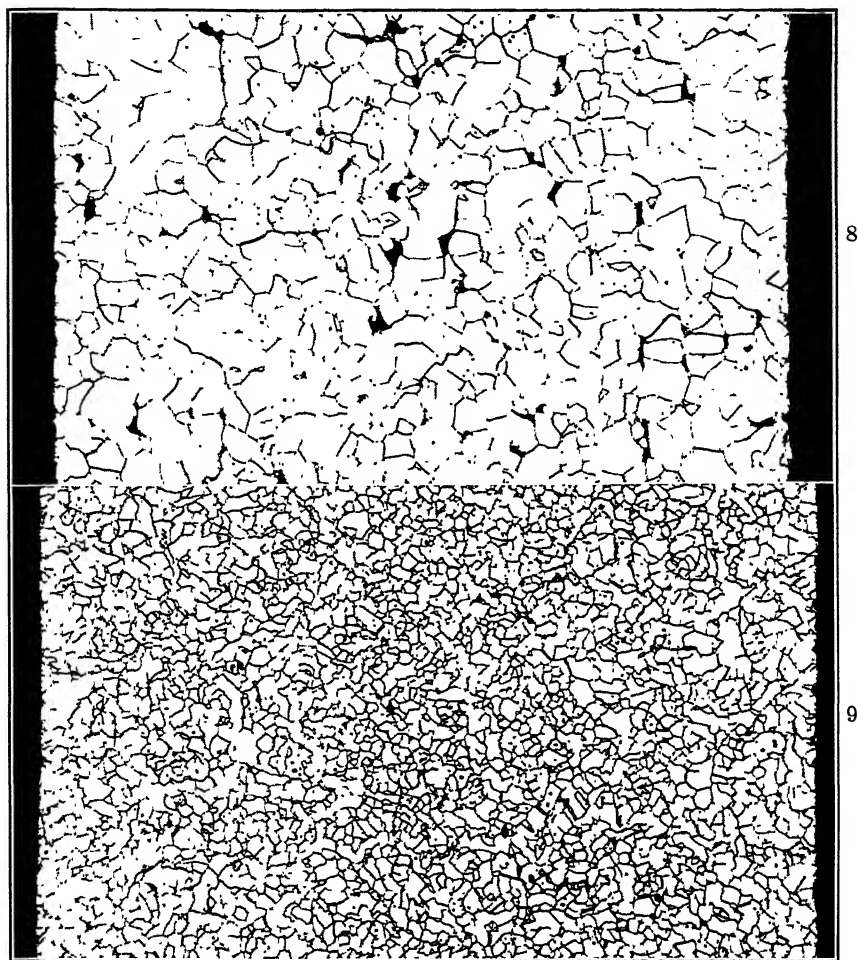
FIG. 8.—FULL CROSS SECTION OF COLD-REDUCED STRIP COOLED IN TUBE FURNACE (40° F. PER MINUTE) FROM 1850° F. AND BOX-ANNEALED AT 1200° F.

FIG. 9.—FULL CROSS SECTION OF COLD-REDUCED STRIP COOLED IN TUBE FURNACE FROM 1850° F., REHEATED TO 1850° F. AND COOLED IN AIR, BOX-ANNEALED AT 1200° F. Both × 100. Specimens etched with nitric acid.

The tensile results after these treatments are given in Table 1 and the corresponding structures are shown by means of photomicrographs (Figs. 7 to 20). In comparing the tensile results with the microstructures, it should be remembered that this type of grain growth is inherently irregular and that truly representative structures have not been photographed. An effort has been made to show the largest grain size in the

TABLE 1.—*Influence of Various Heat-treatments upon Physical Properties of Sheet Steel*

Sample No.	Heat-treatments	Tensile Results		
		Yield Strength, Lb. per Sq. In.	Ultimate Strength, Lb. per Sq. In.	Elongation, Per Cent in 2 In.
284	Box-annealed at 1200° F. in cold-reduced condition. See Fig. 6	39,600	46,300	39
285		39,600	46,900	41
266	Normalized from 1850° F. and box-annealed at 1200° F. See Fig. 7	38,700	46,600	38
267		38,700	46,600	40
272	Cooled in tube furnace[a] from 1850° F. and box-annealed at 1200° F. See Fig. 8	31,100	43,100	38
273		31,100	43,100	39
278	Cooled in tube furnace from 1850° F., subsequently normalized from 1850° and box-annealed at 1200° F. See Fig. 9	36,200	46,300	38
279		36,800	46,000	37
286	Box-annealed at 1375° F. in cold-reduced condition. See Fig. 10	32,600	42,200	41
287		32,000	42,500	41
268	Normalized from 1850° F. and box-annealed at 1375° F. See Fig. 11	34,200	44,600	25
269		34,900	44,400	20
274	Cooled in tube furnace from 1850° F. and box-annealed at 1375° F. See Fig. 12	29,800	42,800	37
275		29,200	43,400	41
280	Cooled in tube furnace from 1850° F., subsequently normalized from 1850° F. and box-annealed at 1375° F. See Fig. 13	33,000	44,400	25
281		31,700	40,600	[b]
288	Box-annealed at 1450° F. in cold-reduced condition. See Fig. 14	30,100	41,200	37
289		31,700	40,800	38
270	Normalized from 1850° F. and box-annealed at 1450° F. See Fig. 15	33,000	42,800	18
271		36,100	44,700	[b]
276	Cooled in tube furnace from 1850° F. and box-annealed at 1450° F. See Fig. 16	30,400	43,100	36
277		30,400	43,100	36
282	Cooled in tube furnace from 1850° F., subsequently normalized from 1850° F. and box-annealed at 1450° F. See Fig. 17	19,000	34,200	15
283		29,800	38,400	[b]

[a] The tube furnace cools at a rate of approximately 40° F. per minute.
[b] Broke outside gauge length.

microsection, and this holds for all samples, both those in which abnormal growth is present and those in which it is not.   The most reliable tensile property for indicating the presence of exaggerated grain growth is elongation.   No elongation values over 25 per cent are found in specimens
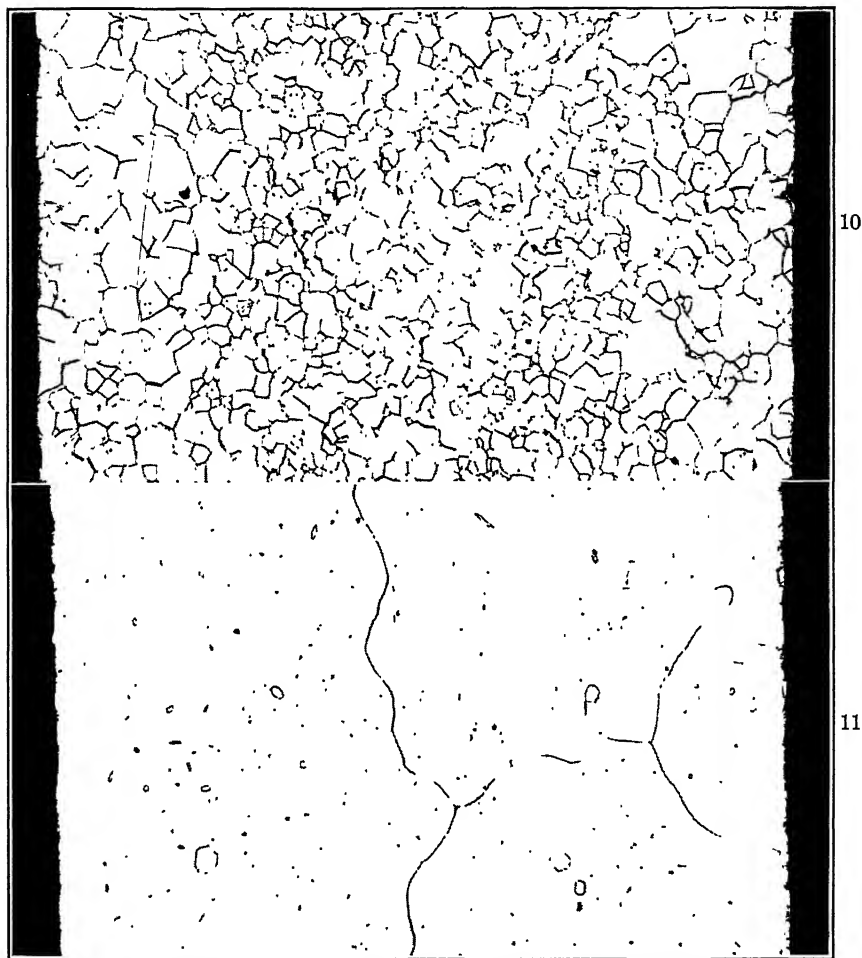
FIG. 10.—FULL CROSS SECTION OF COLD-REDUCED STRIP BOX-ANNEALED AT 1375° F.
IN THE AS-RECEIVED CONDITION.
FIG. 11.—FULL CROSS SECTION OF COLD-REDUCED STRIP NORMALIZED AT 1850° F.
AND BOX-ANNEALED AT 1375° F.
Both × 100.   Specimens etched with nitric acid.

showing such growth, whereas no elongation values less than 36 per cent are found in specimens showing normal grain size.   A comparison of the photographs of the broken tensile samples in Fig. 20 with corresponding tensile data and photomicrographs is helpful in understanding the fact that patches of abnormally large grains embedded in finer grains may

permit fairly good yield and ultimate strength values to be obtained but seriously interfere with elongation.

Response of Cast Material to Normalizing and Box-annealing Treatments.—It was felt at one time that the cause of the growth might be
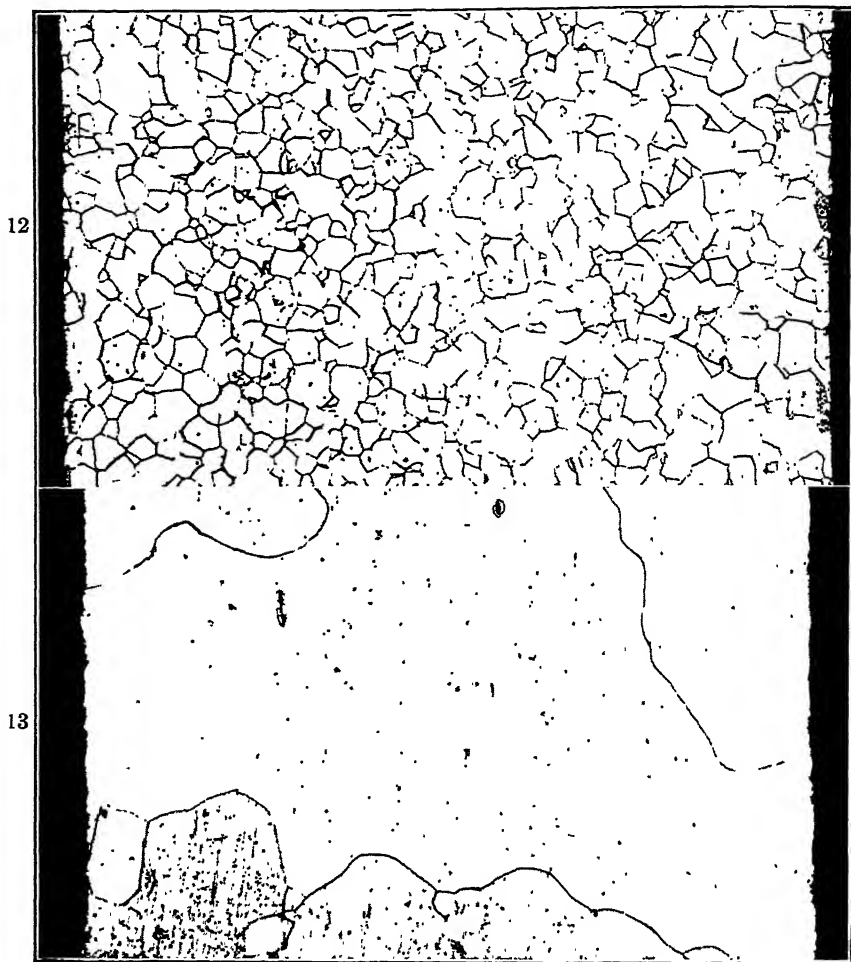
FIG. 12.—FULL CROSS SECTION OF COLD-REDUCED STRIP COOLED IN TUBE FURNACE (40° F. PER MINUTE) FROM 1850° F. AND BOX-ANNEALED AT 1375° F.

FIG. 13.—FULL CROSS SECTION OF COLD-REDUCED STRIP COOLED IN TUBE FURNACE (40° F. PER MINUTE) FROM 1850° F., REHEATED TO 1850° F. AND COOLED IN AIR, BOX-ANNEALED AT 1375° F.

Both × 100.   Specimens etched with nitric acid.

found in residual rolling strains, which may not be completely removed in the normalizing treatment.   In view of this possibility, and to determine, if possible, whether or not there is any relation between the observed

growth and mechanical working—hot or cold—a small ingot was made using an ordinary low-carbon sheet steel as melting stock. The cast material, without any mechanical work whatever, was subjected to the same normalizing and box-annealing treatments as the rolled materials
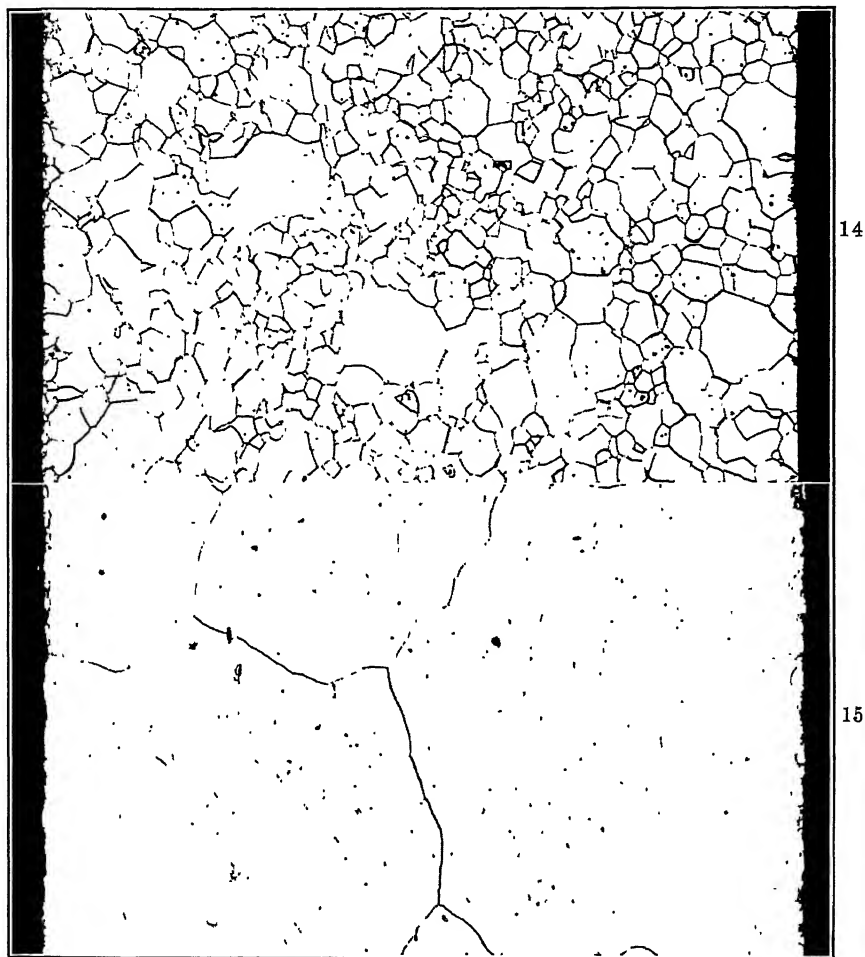
FIG. 14.—FULL CROSS SECTION OF COLD-REDUCED STRIP BOX-ANNEALED AT 1450° F. IN THE AS-RECEIVED CONDITION.

FIG. 15.—FULL CROSS SECTION OF COLD-REDUCED STRIP NORMALIZED FROM 1850° F. AND BOX-ANNEALED AT 1450° F.

Both × 100. Specimens etched with nitric acid.

used in the previous experiments. The structures of the cast, normalized, and normalized box-annealed steels are shown in Figs. 21, 22 and 23, respectively. It is seen here that, while the cast material required a

slightly higher normalizing temperature than usual, it responded to the grain-growth treatment in a manner similar to the rolled sheets.

Response of Killed Steels to the Heat-treatments Previously Outlined.— Specimens of 20-gauge sheets representing 19 different heats made in the
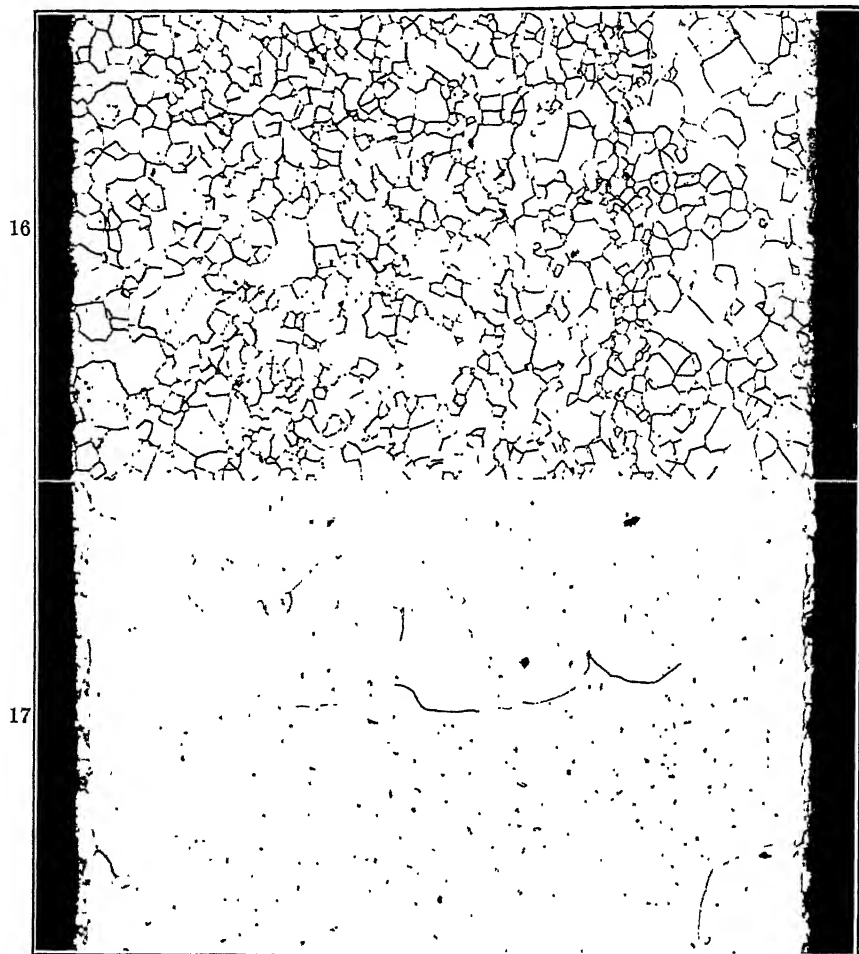
FIG. 16.—FULL CROSS SECTION OF COLD-REDUCED STRIP COOLED IN TUBE FURNACE (40° F. PER MINUTE) FROM 1850° F. AND BOX-ANNEALED AT 1450° F.

FIG. 17.—FULL CROSS SECTION OF COLD-REDUCED STRIP COOLED IN TUBE FURNACE (40° F. PER MINUTE) FROM 1850° F., REHEATED TO 1850° F. AND COOLED IN AIR, BOX-ANNEALED AT 1450° F.

Both × 100. Specimens etched with nitric acid.

15-lb. induction furnace were obtained. These sheets, along with some German-made Izett commercial material, were normalized from 1850° F. and box-annealed at 1450° F. as were the sheet specimens studied previ-

ously. No exaggerated growth took place in any of the specimens from the heats made in the induction furnace but a few cases of typical growth
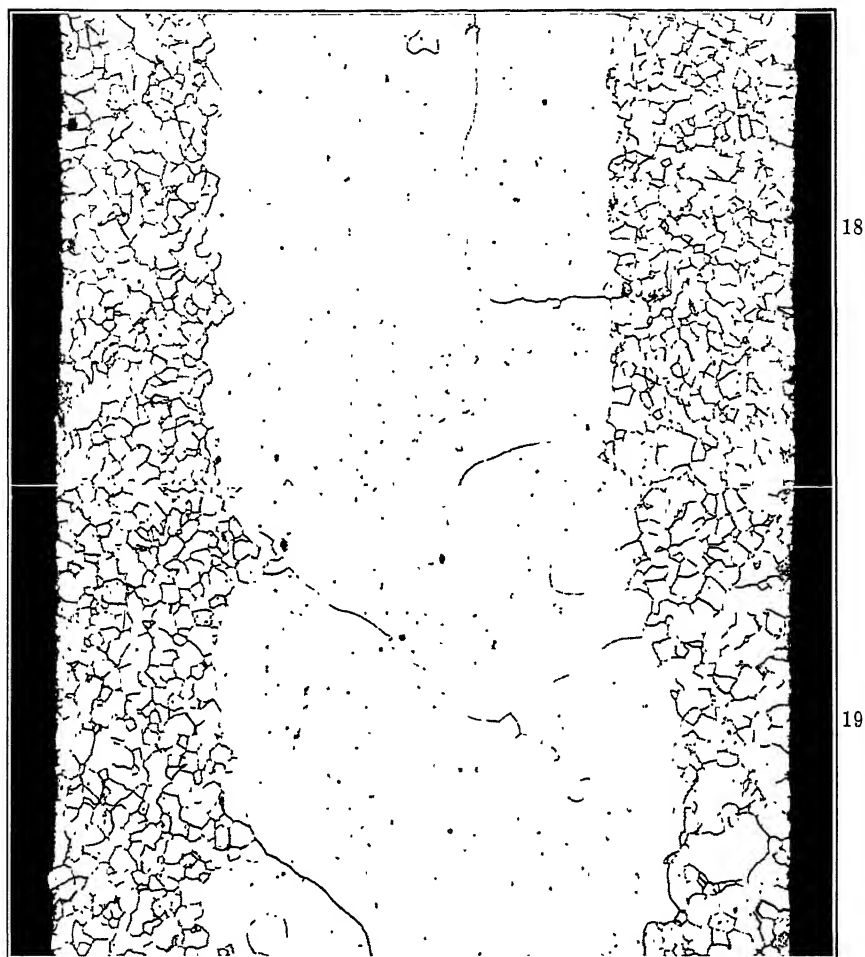
FIG. 18.—FULL CROSS SECTION OF COLD-REDUCED STRIP COOLED IN TUBE FURNACE (40° F. PER MINUTE) FROM 1850° F., REHEATED TO 1850° F. AND COOLED IN AIR, BOX-ANNEALED AT 1450° F.

FIG. 19.—FULL CROSS SECTION OF COLD-REDUCED STRIP COOLED IN TUBE FURNACE (40° F. PER MINUTE) FROM 1850° F., REHEATED TO 1850° F. AND COOLED IN AIR, BOX-ANNEALED AT 1450° F.

These structures indicate that abnormal grain growth in low-carbon rimmed steel is not necessarily accompanied by surface decarburization.

Both × 100. Specimens etched with nitric acid.

were found in the Izett steels. It is not to be concluded from this one experiment that the small heats, necessarily killed, will not respond. Slightly higher normalizing temperatures may be required.

BRIEF SUMMARY OF EXPERIMENTAL RESULTS

The following responses were obtained upon box-annealing at 1375° and at 1450° F.:

1. No growth (abnormal) occurred if the sheet had been heated previously to 1850° F. and cooled in the tube furnace at 40° F. per minute (Figs. 3, 12 and 16).
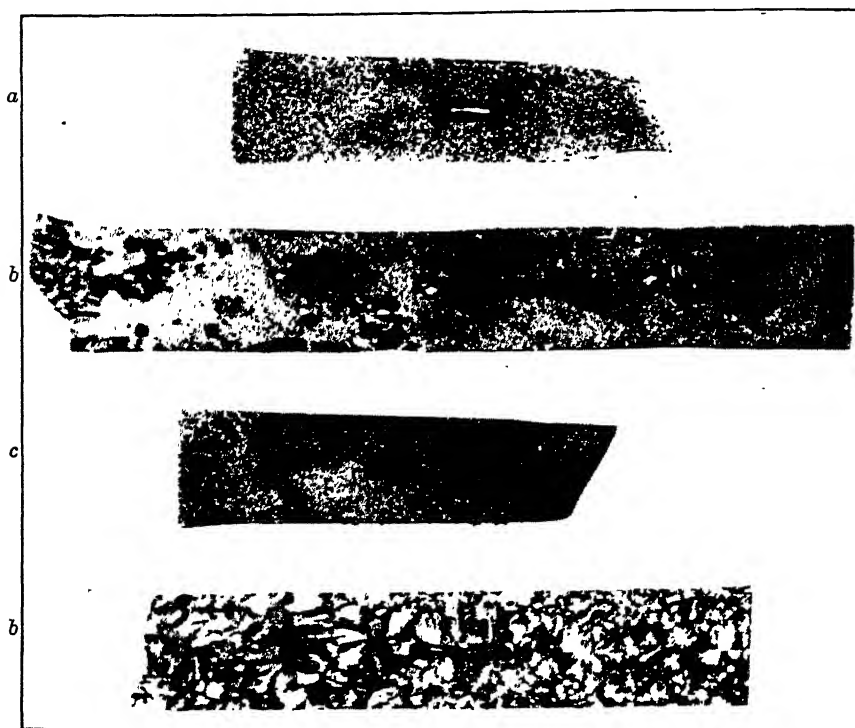
FIG. 20.—TENSILE SPECIMENS AFTER BOX-ANNEALING AT 1450° F.

a. As received, box-annealed.
b. Normalized at 1850° F. and box-annealed.
c. Held at 1850° F. 10 minutes.   Cooled with furnace 40° F. per minute (Globar tube furnace).   Box-annealed.
d. Held at 1850° F. 10 minutes, cooled with furnace (40° F. per minute), reheated to 1850° F. and held 5 minutes, cooled in air and box-annealed.

2. Typical exaggerated growth did occur if the sheets were reheated to 1850° F. and cooled in air (Figs. 4, 13 and 17).   This strongly indicates that the growth is due to something that takes place in the rate of cooling obtained in normalizing the sheet as compared to a cooling rate of 40° F. per minute—that of the tube furnace.

3. Cooling rates between normalizing and 40° F. per minute produced a graded series as regards growth, greatest growth resulting from the fastest cooling.

4. Cooling in air from temperatures slightly above to slightly below the point of maximum transformation (Ar₃) resulted in no growth. Quenching from temperatures slightly above the temperature of maximum
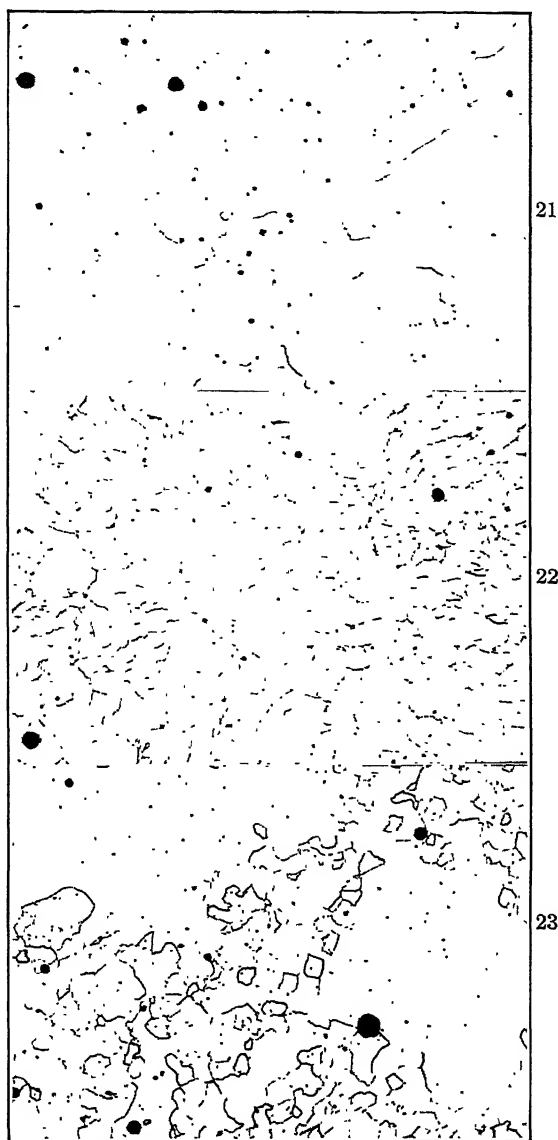
FIG. 21.—CAST STRUCTURE OF ORDINARY SHEET STEEL HAVING FOLLOWING COMPOSI-
TION BEFORE REMELTING: C, 0.07; MN, 0.38, P, 0.012; S, 0.024.
FIG. 22.—STRUCTURE OF STEEL SHOWN IN FIG. 22 AFTER NORMALIZING FROM 1950° F.
FIG. 23.—STRUCTURE OF STEEL SHOWN IN FIG. 23 AFTER BOX-ANNEALING AT 1450° F.
NOTE TYPICAL EXAGGERATED GROWTH.
All × 100.   Specimens etched with nitric acid.

transformation resulted in some abnormal growth while quenching from a temperature slightly below this point resulted in no growth (Fig. 5).

5. Cast material that had been previously normalized from 1950° F. gave typical abnormal grain growth (Figs. 21, 22 and 23). This removes the possibility of residual rolling strains as a growth stimulus.

6. Specimens from several killed heats made in a 15-lb. induction furnace did not show growth after normalizing from 1850° F. (Data rather incomplete, as only one box-annealing cycle was carried through.)

7. Specimens of commercial Izett steel did show typical growth in a few cases after normalizing from 1850° F.

8. Growth usually occurs in the skin or rim zone of the sheet but the exceptions are too numerous to be classed as accidental (Figs. 18 and 19).

DISCUSSION OF POSSIBLE CAUSES OF GROWTH

The producers of sheet steel have long known that sheets normalized in furnaces with no cooling chambers could not subsequently be annealed at temperatures as high as could sheets finished on the hot mills. Straight normalized sheets are rarely box-annealed at temperatures higher than 1250° F., whereas the hot-finished material is usually annealed at 1350°, or even 1450° F. if a very soft product is desired. It is hoped that the experiments reported in this paper have made clear the distinction between abnormal grain growth following mechanical straining and that following normalizing treatments. A discussion of the *causes* of such growth must necessarily be speculative in character but is of interest nevertheless.

While much is known about the conditions attending abnormal grain growth during the low-temperature annealing of strained ferrite, the entire literature on the subject of exaggerated grain growth following certain heat-treatments, or to use one author's terms, "growth in the absence of strain," so far as the present writer knows, is limited to three papers, all of which are recent. In 1933 Kinsky[16] wrote that:

Such cooling (normalizing) seems to produce in alpha iron a small non-uniformly distributed thermal intercrystalline strain, which is not removed during the process of annealing. This thermal strain may be regarded as the cause of abnormal growth after box annealing. The explanation offered is in full accord with the influence of mechanical strain on grain growth.

In a recent paper McCarthy[17] observed that in some instances the rim of the rimmed-steel samples coarsened in the area that had received no cold-work:

To establish this definitely a sample of Steel A was heated to 1700° F. to remove all traces of strain resulting from cold work, and cooled in air. It was then heated to 1350° F. for 24 hours. As a result the grains in the rimmed area grew enormously. This accounts for the grain growth often observed in the rim of annealed low carbon wire made by the rimming process. No abnormal growth was observed in the center.

McCarthy leaves the subject with the statements that:

Grain growth can occur in the rim of rimmed steels in the absence of strains at a temperature of 1350° F. The reason for this is not quite apparent. That it is not due to the degree of purity alone is demonstrated by the fact that electrolytic iron, which is more pure, does not grow on heating to the same temperature.

It is probable that McCarthy's normalizing treatment to "remove all traces of strain resulting from cold work," predisposed the steel to abnormal grain growth.

The third reference to the subject is a paper by a German investigator,[18] in which it is stated that an occasional grain coarsening appeared to be associated with rapid cooling from the normalizing temperature. This effect was explained on the basis that foreign particles remain in solution on rapid cooling and, therefore, cannot hinder grain growth. Along this line of reasoning, one would say that in our experiments many foreign particles are taken into solution at 1850° F. and that during subsequent rapid cooling, as in normalizing, not enough precipitation occurs to give the critical amount and size of particles to obstruct growth; hence germination occurs upon subsequent box annealing. When slower cooling rates are followed, as in the tube furnace, precipitation again takes place to such an extent that the germinative temperature is raised above our maximum box-annealing temperature.

The theory of thermal strains as a cause for such growth, which Kinsky suggested, should be given careful consideration since it fits in so perfectly with the same type of growth following cold-work. Thermal strains sufficient to rupture high-carbon steels are, of course, frequently met with when the gamma-to-alpha transformation is forced to take place at very low temperatures. This, however, is quite different from the normal air cooling of a low-carbon sheet in which the transformation probably occurs while there is still considerable plasticity present.

The response of the sheets to the quenching treatments from temperatures ranging around the Ar_3 point may be taken as a strong indication that the rapidity of the transformation is the controlling factor. The Ar_3 point is, of course, not truly a "point" but is simply a mark of the temperature at which maximum separation occurs for the particular cooling rate of this furnace. The presence of abnormal growth in specimens quenched from a temperature slightly above the Ar_3 point may come about through the introduction of thermal strains, but it must also be remembered that a difference in solubility of foreign particles (possibly FeO) in alpha and gamma iron may exist; in fact, the red-shortness of low-metalloid steels over a certain temperature range is conveniently explained on this basis.

It seems possible that a lever relationship may exist between growth forces and forces tending to prevent growth. Fig. 24 shows the conditions necessary for abnormal grain growth—a delicate balance between

growth forces and those of inertia, with a slight advantage in favor of the growth forces.

It seems certain that the normalizing treatment increases virtually every one of the factors tending to cause growth. It may also influence the other end of the lever through its effect on the nonmetallic foreign particles or grain-growth obstructions. Such particles are known to be unevenly distributed as regards the core and the rim of sheet steels and the abnormal growth tendencies also often vary in the same way, as Figs. 1, 18 and 19 indicate.

The abnormal growth in the core portion of the sheets as shown in Figs. 18 and 19, accompanied by normal grain size in the rim or skin part, might be taken as an indication that the obstruction particles are too few in the rim but are optimum as to size and distribution in the core. Usually one finds the optimum condition for abnormal growth in the rim and

Forces of inertia

| 1 | (1) Rigidity-function of temperature |
| 2 | (2) Obstructions |

Growth forces

1	(1) Crystal size
2	(2) Crystal form
3	(3) Surface condition
4	(4) Distortion
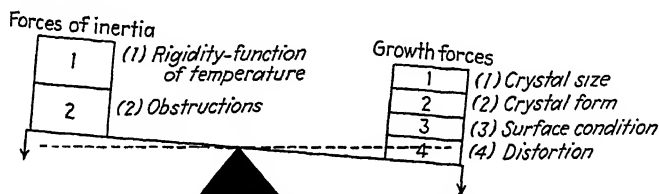
FIG. 24.—CONDITIONS NECESSARY FOR ABNORMAL GRAIN GROWTH.

inertia forces too great in the core for germination to occur there. Here again, however, it is to be remembered that the variation of carbon content from rim to core would undoubtedly produce some difference in thermal stresses as regards these two regions after the normalizing treatment.

ACKNOWLEDGMENT

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DISCUSSION

(Cyril Wells presiding)

J. H. NEAD,* Indiana Harbor, Ind. (written discussion).—It would be interesting to know what the structures of the samples listed in Table 1, were before box annealing and after the several heat-treatments from 1850° F. It is probable that the normalizing or rapid cooling from 1850° F. set up internal strains in the samples, which resulted in abnormal grain growth during subsequent box annealing. It is possible that evidence of such strains may be found by X-ray analysis, and that this method of investigation of the samples after the 1850° F. heat-treatments would be of interest. Also, it would be interesting to examine in this manner samples that were heated above 1850° F. and then cooled rapidly to just below the A_1 point and subsequently slowly cooled and the reverse treatment that is heated above 1850° F. and slowly cooled to below the A_1 point followed by rapid cooling to atmospheric temperature.

C. C. MAHLIE,† Indiana Harbor, Ind. (written discussion).—The following comments are made after a hasty review of the paper: It is unfortunate that X-ray was not used in conjunction, primarily to determine amount of strain after normalizing. What was the cooling rate of this treatment?

It would have been interesting to have this work supplemented by cold reduction of strain-free sheets to determine what amount of cold reduction would be necessary to give same grain growth as the author obtained on the normalized sheets on box annealing. X-ray examination of these pieces for comparison of amount of strain before annealing would have been interesting.

The author did no annealing between 1200° and 1375° F. (right in the commercial range). Results shown in Figs. 8 and 12 certainly show enough difference to warrant further investigation between these two temperatures.

Small surface grains, Figs. 16 and 18, are interesting.

I believe the author would have found the strain about the same, whether introduced by cold reduction or air quenching.

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* Chief Metallurgist, Inland Steel Co.

† Assistant Chief Metallurgist, Flat Rolled Products Division, Inland Steel Co.

K. L. KERSCHBAUM,* Indiana Harbor, Ind. (written discussion).—This paper clearly shows that an abnormal grain growth can take place in a normalized steel during subsequent box annealing, provided the cooling rate from the previous normalizing temperature is not controlled. This explains why it has been almost impossible to get a complete correlation between laboratory and production heat-treatments and processings.

The author's explanation of the forces controlling crystal growth seems to fit in nicely with results obtained in plant practice. As the cooling rate becomes slower—that is, below 40° F. per minute—will the grain be progressively smaller after box annealing, and can higher temperatures be used in box annealing without abnormal grain growth?

We have found that various rapid coolings from normalizing temperatures result in a much harder material, and with the most severe quench the microstructure was markedly changed. It is probable that the small amount of carbon present in these samples was in solid solution. However, since the carbon was below 0.10 C., we feel that a part of the quench hardness is due to internal strains, since the material is going through dilatometric changes at the time of quenching. It is regrettable that the micro samples were etched so heavily that the carbide conditions cannot be studied.

That some of the abnormal grain growth could be attributed to either the carbon condition or to dilatometric changes is indicated by the experimental results, since abnormal growth on subsequent box annealing was indicated on air quenching above 1590° F. or water quenching above 1515° F. Quenching or rapid cooling during passage through the A_3 should lock up internal strains, which would upset the equilibrium enough for abnormal grain growth to take place during a subsequent box annealing.

It is interesting that the hot-rolled material, cold strip, and cast low-carbon steel all showed the same response to box annealing after controlled cooling from 1850° F. and all showed abnormal grain growth on box annealing if the cooling from the 1850° F. normalizing temperature was rapid. We believe, though, that by controlling the box annealing after a rapid cooling a uniform open grain can be obtained.

The author found that a low-carbon killed steel was not so susceptible to the type of abnormal growth shown by the rimmed samples. Perhaps the Izett steel, used as a comparison, was not as fully killed. Was any of this particular Izett checked for aging? It might well be that there is some connection between nonaging and the forces that offer resistance to abnormal grain growth. It would be interesting to know why the electrolytic iron mentioned by one of the authors, and used as a reference, did not show abnormal grain growth, since, presumably, it is an aging material. The various explanations offered by others regarding this type of abnormal grain growth have points of merit, and the present explanation is plausible because it fits in nicely with the experimental results. However, we believe it would be interesting to re-study the micro specimens with respect to the carbide conditions.

R. L. RICKETT,† Kearny, N. J. (written discussion).—This paper presents experimental results that are very interesting and of considerable practical importance. The work would be of greater practical value, however, if it had been extended to include a more thorough investigation of the box-annealing temperature range 1000° to 1300° F., which is probably more commonly used for box-annealing *normalized* low-carbon steel sheet and strip than the higher temperatures used by the author in most of his work. The effect on grain growth of soaking for longer than a 3-hr. period in this lower temperature range would be of particular interest.

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* Metallurgist, Flat Rolled Products Division, Inland Steel Co.
† Research Laboratory, United States Steel Corporation.

The results given in Table 1 would be more easily comprehended if presented in graphic form. Of the three annealing temperatures for which data are given in this table, only 1375° and 1450° F. caused exaggerated grain growth in previously normalized material; both of these are above the A_1 temperature and consequently resulted in complete solution of the carbide present. It would be interesting to know whether such solution of the carbide during a part of the box-annealing cycle is necessary to produce very coarse grains in previously normalized material, or whether exaggerated grain growth would occur if the steel were held at a temperature below A_1 for a considerable period of time.

The author's experiments in which specimens were air-cooled from various temperatures (after furnace cooling from 1850° F. to the desired temperature) indicate that it may be possible by normalizing at some temperature below 1850° F. to avoid marked grain growth on subsequent box annealing at 1450° F. His work on the effect of cooling rate during various portions of the "normalizing" cycle indicates that the grain-growth behavior on subsequent box annealing is influenced not only by the cooling rate below what he designates as the "A_3 temperature" but also by the cooling rate from 1850° F. to the "A_3 temperature."

M. L. SAMUELS (written discussion).—In answer to Mr. Nead's question, it may be stated that where no abnormal grain growth took place during box annealing, no visible change in the grain size was observed. Fig. 7, therefore, represents the grain size after air cooling from 1850° F., and Fig. 8 represents the structure after cooling in the tube furnace. The low box-annealing temperature of 1200° F. did not spheroidize the pearlite (see Fig. 8) nor change the grain size at all.

Mr. Mahlie's question as to cooling rates during normalizing cannot be answered by stating the rate in degrees per minute. The cooling rate was that of a $\frac{3}{16}$-in. (0.187-in.) strip and a 20-gauge (0.037-in.) sheet quickly removed from the furnace and held in still air.

Mr. Kerschbaum's question as to the effect of cooling rates slower than 40° F. per minute upon final grain size after box annealing is important, since it bears upon one difference between structures originating from cold reduction followed by box annealing, and normalizing followed by box annealing. Upon box-annealing heavily cold-reduced sheets at a given annealing temperature, say 1300° F., it is found that the final grain size varies with the degree of cold deformation, provided no abnormal grain growth occurs. The greater the cold reduction, the finer will be the grain size after box annealing. Also, for a given cold reduction, the grain size after box annealing varies with the maximum annealing temperature, again with the provision that abnormal growth is absent. The higher the annealing temperature, the larger will be the grain.

Upon box-annealing normalized sheets, provided abnormal grain growth is not encountered, no comparable change in grain size is produced by the box-annealing treatment. The hardness of the sheet is markedly reduced, probably through agglomeration of finely dispersed carbide particles, but the grain size before and after box annealing of the normalized sheet is very nearly the same if the annealing temperature is not high enough to produce abnormal growth. The control of the grain size in this case is obtained by controlling the rate of cooling through the transformation range during normalizing. Figs. 8, 12 and 16 show almost identical grain sizes after being box-annealed at 1200°, 1375° and 1450° F., respectively. A change in the rate of cooling through the transformation range is an entirely different story.

In this paper an effort has been made to separate mechanical straining and thermal treatments as stimuli for abnormal grain growth. Nothing original is claimed, and credit for the observation of the phenomenon is given to Kinsky. It has been demonstrated here, however, that abnormal grain growth can be induced through heat-

treatment alone and in the absence of cold-work. In trying to think of the causes of such growth, the writer has again given the views of previous authors, which include two causes for such growth: (1) the introduction of strains in the steel, which originate both from the change in volume in passing from the gamma to the alpha form and from strictly thermal stresses; (2) a change in the form and distribution of grain-growth inhibitors during the heat-treatment prior to box annealing.

The writer has been criticized by others than the discussers of this paper for including a supplementary factor in addition to thermal strains as a possible cause for abnormal growth. Certainly no one will deny that thermal strains in the sheets would be found after normalizing if they were examined through the use of X-rays. The effect of an inhibitor—thoria—in grain-growth control in tungsten will be admitted by all, while most metallurgists think aluminum oxide exerts a certain control of abnormal grain growth (the growth of a few grains at the expense of their smaller neighbors) in austenite. The preferential growth of grains in the rimmed or skin zones in wire, sheet and strip steel may be taken as indirect evidence, since such preferential growth is more easily explained by supposing a difference exists in the distribution of nonmetallics in the skin portion and the center or core of the original ingot than by assuming a difference in thermal strains between the two zones. The skin part of the ingot is subjected to the sweeping action of the gas evolved during rimming, while the core portion solidifies after capping and can be looked upon as a small killed ingot inside the large one in so far as inclusions are concerned.

If Mr. Nead could only go on and give a clear picture of just how mechanical or thermal strains act in producing growth, much that is now obscure as to the nature of plastic deformation and recrystallization might be cleared up. Sir William Bragg, who probably knows as much about X-ray investigation as any other worker in this field, has recently pointed out the need for a method of studying structures and particles ranging in size from those too small for the microscope but rather too large for X-ray study—inframicroscopic magnitudes. The microscopist speaks of resolving particles as small as a few hundred Ångstrom units in diameter, but detail is absent from such observations. There is an enormous void existing between magnitudes sufficiently large for a detailed study by means of the microscope and those small enough for X-ray investigation.

Mr. Rickett's criticism for not including lower box-annealing temperatures is certainly justifiable, and it is hoped that further work can be carried out along this line. The extent of the work reported in the present paper had to be limited, and, since the main purpose was to try to see whether abnormal grain growth could be produced in the absence of mechanical straining, the higher temperatures for box annealing were used.

The question of showing graphically the effect of cooling rate upon grain size developed in subsequent box annealing was considered, but it was felt that not enough data were available. If we were working with an effect that is inherently uniform— such, for example, as the relation between finishing temperature in the rolling of medium carbon rods and the resulting grain size—a few tests would be significant. Abnormal or exaggerated grain growth is notoriously irregular, and many tests would have to be made before such a graph could be constructed, and even then it would be of questionable value. Only those who have worked with the routine inspection of sheets for deep-drawing purposes can fully appreciate the vagaries of abnormal grain growth.

Temperature-gradient Studies on Tempering Reactions of Quenched High-carbon Steels

By Charles R. Austin* and B. S. Norris†

In a recent paper the authors[1] discussed the reactions to tempering of hypereutectoid steels quenched from 1000° C., as revealed by studies on changes in hardness, electrical resistivity, coercive force and metallographic characteristics. The data, which related specifically to tempering temperatures of 550°, 650° and 710° C., for varying periods up to 125 hr., permitted the following important conclusions:

1. The rate of softening of the steels at the temperatures examined differed markedly although the steels were of "similar" general chemical composition.

2. The temperature of maximum softening spread over a range from about 650° C. to the eutectoid inversion.

3. The divergence in behavior was ascribed, at least in part, to a profound difference in tendency to graphitization on annealing at subeutectoid temperatures.

4. The mode of spheroidization of the cementite, as revealed by metallographic studies, also varied considerably in the different steels.

The purpose of the present investigation is to pursue further the study of the difference in behavior of the steels on tempering over a wider range of temperature. To this end the following features have received particular attention:

1. Comparison of temperatures of maximum softening of the various steels when the quenched samples were tempered for 5 hr. and for 75 hr. followed by furnace cooling and by quenching in water.

2. Determination of the effect of quenching temperature, prior to tempering, on the rate of softening. Quenching temperatures of 1000° and 850° C. were used in the investigations.

3. Examination of the microstructures obtained with the various heat-treatments employed.

Since the softening of the steels was frequently largely controlled by graphitization, these studies are naturally very much concerned with this phenomenon.

In order to extend the "tempering" treatments above the temperature of the eutectoid transformation, the heat-treatments ranged from about 450° to 800° C.

MATERIALS AND EXPERIMENTAL PROCEDURE

The steels used in the investigation were identical with those discussed in the previous paper, and represented the commercial products of three different steel companies. The type of steel and chemical analyses are recorded in Table 1.

TABLE 1.—*Chemical Analysis of the Steels*

Type of Steel	Steel	Composition, Per Cent										
		C	Mn	Si	P	S	Cr	Ni	Va	Cu	Al	Al₂O₃
O.H.	A	1.09/1.09	0.31	0.27	0.018	0.031	0.12	0.06	Nil	0.16	0.005	0.010
E.F.	B	1.04/1.05	0.30	0.44	0.028	0.025	0.05	0.06	Nil	0.12	0.000	0.009
E.F.	C	1.12	0.25	0.30	0.019	0.013	0.11	0.07			0.005	0.010
O.H.	D	1.00/1.00	0.42	0.17	0.016	0.027	0.09	0.12	Nil	0.10	0.011	0.008
O.H.	E	0.98/0.98	0.40	0.21	0.013	0.031	0.03	0.08	Nil	0.08	0.000	0.009
E.F.	F	1.00/1.00	0.32	0.27	0.009	0.018	0.06	0.16	Nil	0.08	0.025	0.008

The chemical analyses previously reported were supplied by the manufacturers and represented the analysis of the various heats. The authors are indebted to Mr. G. V. Luerssen, of the Carpenter Steel Co., for the chemical analyses now reported. The data refer to the actual ⅜-in. bar stock on which the investigations were conducted.

The analyses for alumina and metallic aluminum have also been rechecked, through the courtesy of Mr. H. W. McQuaid, of the Republic Steel Co., and are now reported as accurate to ±10 per cent. The values are considerably lower than those given in the earlier paper.

The effects of tempering the quenched steels were determined from hardness measurements and from studies of microstructural changes in the steels. The complete series of heat-treatments is given in Table 2. Steel A was included in all test runs, as a check on duplication of heat-treatment.

Hardening.—All material was in the form of ⅜-in. bar stock. Samples 12 in. long were heated to the desired temperature, maintained for 1 hr. and quenched in cold water. The heating was done in an electrically heated tube furnace, where the temperature variation did not exceed ±5° C. All samples treated for quenching in any given run were subsequently tempered at the same time. Similarly, all specimens annealed

for quenching at one time (a maximum of four) were simultaneously quenched in water. Complete hardening was evident from the fracture of the hardened bars.

TABLE 2.—*Complete History of Heat-treatments of Steels and Coordination of Samples in Runs*

Run No.	Steels	Prequenching		Time in Gradient Furnace, Hr.	Method of Cooling from Gradient Furnace
		Temperature, Deg. C.	Time at Temperature, Hr.		
1	A,B,D	1000	1	5	Water quench
2	A,E,F	1000	1	5	Water quench
3	A,B,D	1000	1	5	Furnace cool
4	A,E,F	1000	1	5	Furnace cool
5	A,B,C,D	1000	1	75	Water quench
6	A,E,F	1000	1	75	Water quench
7	A,B,C,D	1000	1	75	Furnace cool
8	A,E,F	1000	1	75	Furnace cool
9	A,B,D	850	1	75	Furnace cool
10	A,E,F	850	1	75	Furnace cool

Most of the quenched test samples were obtained from an anneal at 1000° C. in conformity with the data submitted in the previous paper. However, a series of quenchings from 850° C. was included in order to determine the importance of the high-temperature quench on the data from subsequent heat-treatment.

Tempering.—In order to obtain a complete history of the effects of tempering the quenched bars, over a wide range of temperature (450° to 800° C.), the 12-in. bars were annealed in a gradient furnace, so constructed that a uniform rate of change in temperature was obtained over almost the entire length of the bars, and a strictly linear relationship appeared to hold from about 500° to 760° C.

After tempering or annealing for the desired time (5 or 75 hr.) the batch of specimens was allowed to cool in the furnace or was quenched in water, in accordance with the treatment designated in Table 2. The tempering operation usually was started within one hour after the samples had been quenched.

Hardness Determinations.—After final heat-treatment, diametrically opposite flat surfaces were machined or ground lengthwise along the bars. Usually it was sufficient to cut to a depth of $\frac{1}{16}$ in. but sometimes it was necessary to increase the cutting to $\frac{1}{8}$ in. in order to ensure the removal of any partially decarburized material. Naturally, the latter condition was observed only at temperatures above the eutectoid transformation. The machined or ground surface was then prepared for hardness tests by use of emery papers, with a final grinding on 1/0 paper.

On account of cracking during quenching and concomitant decar-burization, fine polishing and etching were used in certain instances, in order to obviate spurious hardness readings, particularly in the portions of the bars "tempered" above the eutectoid inversion.

Hardness readings were observed at ¼-in. intervals along the length of each specimen, by use of the Rockwell B scale. For sections water-quenched from above the critical, Rockwell C was employed. Both
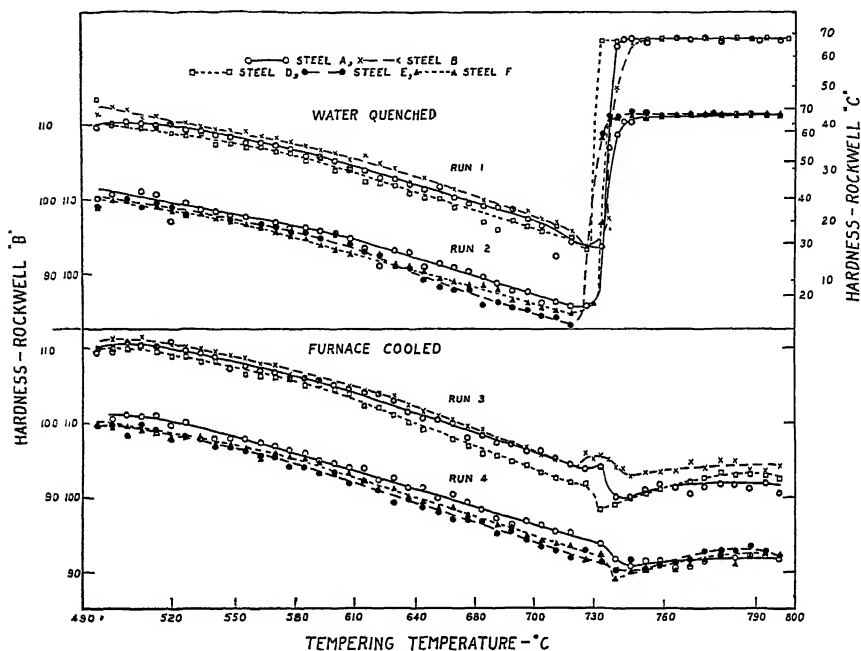
FIG. 1.—DISTRIBUTION OF HARDNESS DATA FROM FIVE HYPEREUTECTOID STEELS TEMPERED 5 HOURS IN A GRADIENT FURNACE (500° TO 800° C.) AFTER QUENCHING FROM 1 HOUR AT 1000° C. RUNS 1 AND 2, WATER-QUENCHED AFTER TEMPERING. RUNS 3 AND 4, SLOWLY COOLED IN GRADIENT FURNACE AFTER TEMPERING.

scales were used in the intermediate hard zone in order to permit a strict correlation of the two scales.

RESULTS OF HARDNESS DETERMINATIONS

The data obtained from hardness determinations of quenched bars after annealing in a gradient furnace are presented in the form of graphs in Figs. 1 to 6.

In the published research on these steels, a plot was made of Rockwell hardness B against the logarithm of the tempering time in hours from ½ hr. to 125 hr. for the tempering temperatures 550°, 650° and 710° C. All steels exhibited a linear ratio up to 5 hr. tempering. When the time of treatment was increased the linearity persisted in some of the steels, but in others the hardness began to drop sharply.

Fig. 1 illustrates the behavior of the steels on tempering over a wide temperature range (500° to 800° C.) for 5 hr., after quenching from 1000° C. The curves indicate the general similar nature of response to softening, when the tempering is followed by either water-quenching or slow cooling in the gradient furnace. The hardness decreases in an approximately linear ratio with temperature. However, steel E, which has the lowest carbon content, appears to soften a little more than the other samples when tempered above 600° C. The break in the curve is evident in the sample quenched from the tempering temperature (run 2).
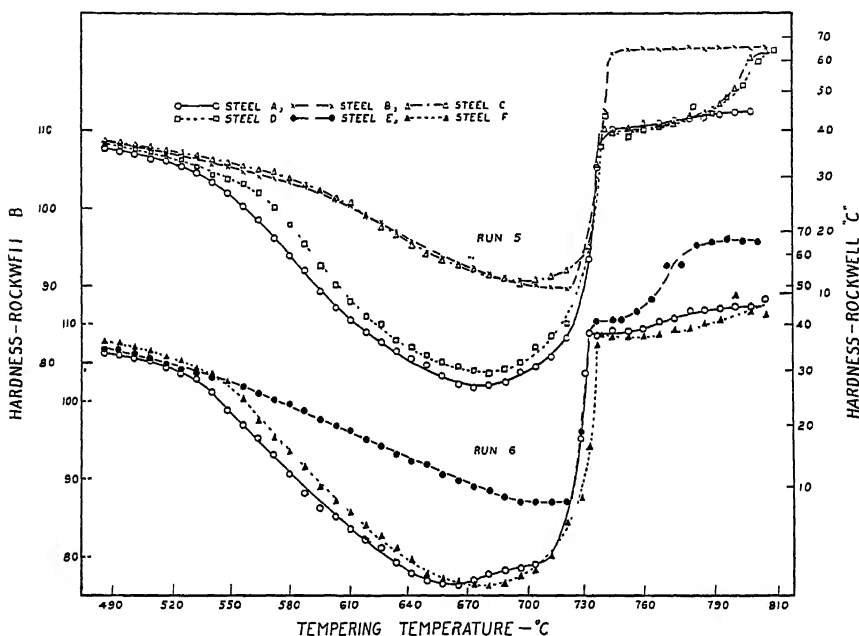
FIG 2.—DISTRIBUTION OF HARDNESS DATA FROM SIX STEELS TEMPERED 75 HOURS IN GRADIENT FURNACE (500° TO 800° C.) AFTER WATER-QUENCHING FROM 1 HOUR AT 1000° C. All steels were water-quenched subsequent to tempering.

There appears to be a spread of approximately 10° C. in Ae₁ eutectoid inversion but all steels reach a maximum quenched hardness of 66 Rockwell C.

In the furnace-cooled steels the hardness data below the lower critical point are little different from those of the quenched samples. At the critical there appears to be a small but real drop in hardness, except in steel B. Above the critical, a general slight increase in hardness obtains, steel B maintaining its superior position.

Fig. 2 depicts the reaction to tempering (500° to 800° C.) for 75 hr. after water-quenching from 1 hr. at 1000° C. All samples were also water-quenched subsequent to the 75-hr. treatment. A natural division
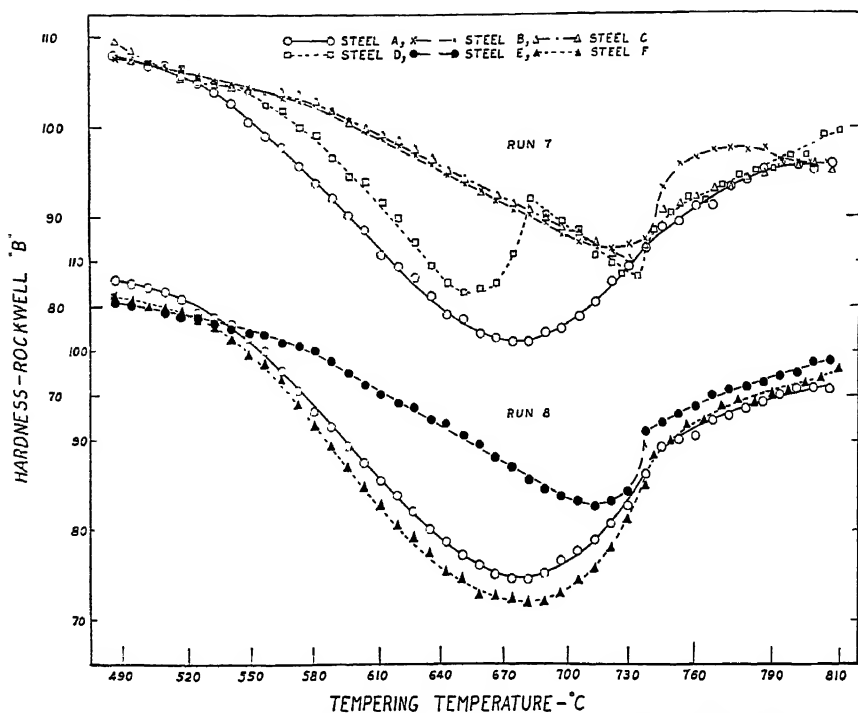
FIG. 3.—DISTRIBUTION OF HARDNESS DATA FROM SIX STEELS (SAME AS FIG. 2) TEMPERED 75 HOURS IN GRADIENT FURNACE AFTER WATER-QUENCHING FROM 1 HOUR AT 1000° C.

All steels were slowly cooled in gradient furnace subsequent to tempering.
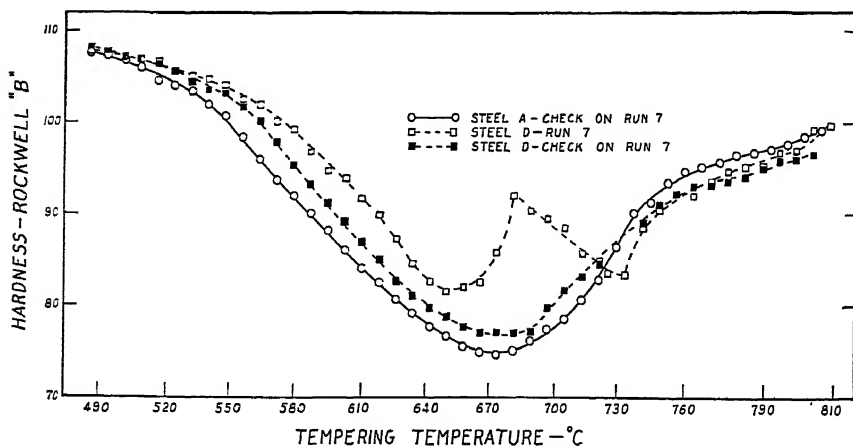
FIG. 4.—CHECK ON DISTRIBUTION OF HARDNESS DATA FROM STEEL D (SEE FIG. 3) TEMPERED 75 HOURS IN GRADIENT FURNACE AFTER WATER-QUENCHING FROM 1 HOUR AT 1000° C.

Steel was slowly cooled in gradient furnace subsequent to tempering.

of the steels into two groups, B, C, E, and A, D, F, is now evident.   In the second group steels D and F, and one sample of A, show a minimum
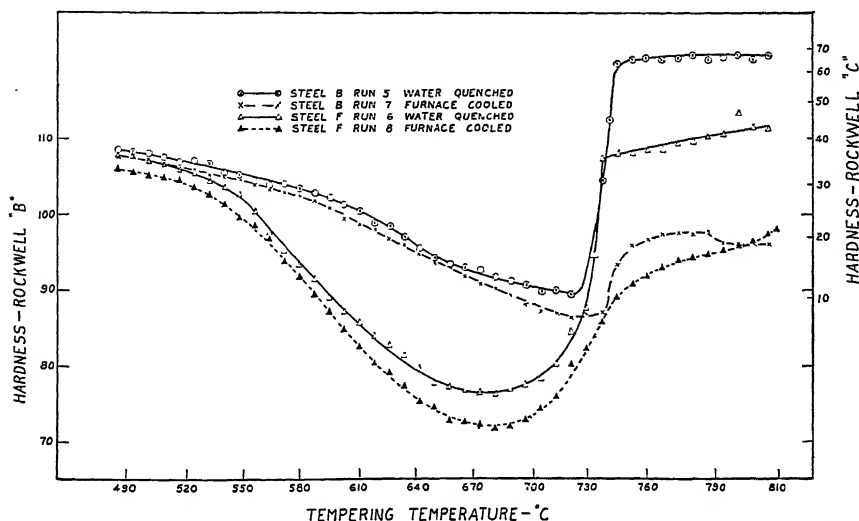
FIG. 5.—DISTRIBUTION OF HARDNESS DATA FROM STEELS B AND F FOR FINAL WATER-QUENCHING AND FURNACE-COOLING.
Steels were quenched from 1 hour at 1000° C. prior to tempering for 75 hours.
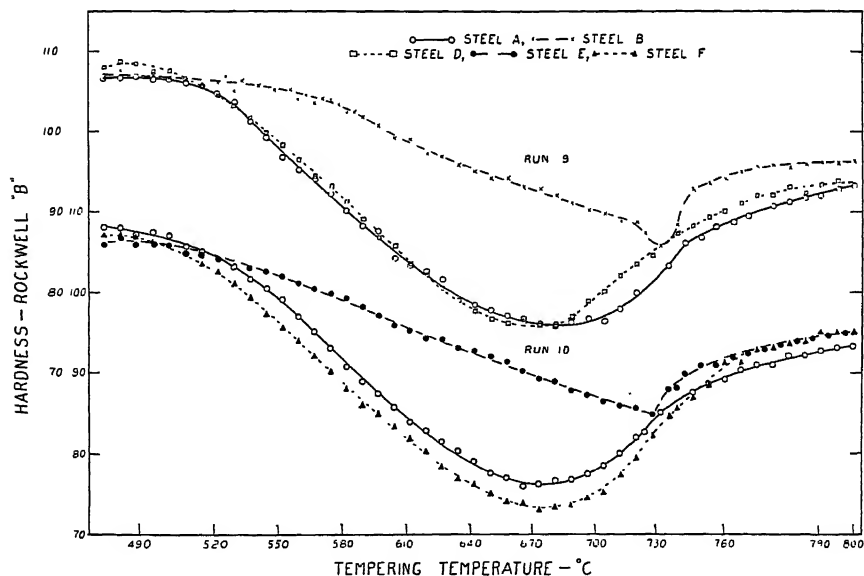
FIG. 6.—DISTRIBUTION OF HARDNESS DATA FROM FIVE STEELS TEMPERED 75 HOURS IN GRADIENT FURNACE AFTER WATER-QUENCHING FROM 1 HOUR AT 850° C.
Steels were slowly cooled in gradient furnace subsequent to tempering.

hardness at 680° C. whereas the other sample of A has a minimum at 660° C., followed by a slight hump between 670° and 700° C.   The first

group exhibits a minimum a little short of the lower critical point (700°
to 720° C.), but the maximum degree of softening is very different in the
two groups.

The particularly interesting feature is the striking similarity in
tempering behavior of the three steels within any one group.

After 5 hr. "tempering" above the critical all the steels reacted
identically on quenching (Fig. 1), whereas after 75 hr. treatment there are
now considerable differences.   Group B, C, E attains a fully hard condi-
tion of Rockwell 65 C when quenched from about 800° C., but only steel
B hardens fully on quenching from temperatures slightly above the A₁
critical.   Steel E is intermediate in behavior and completely hardens
after a temperature of 780° C. is exceeded.   It is important to point out
that the previous research has shown that both B and E have the greatest
tendency to coarsening of the austenitic grain.   The reason for the lack of
hardenability of steels A and F and the peculiar shape of the super-
eutectoid curves of steel D and steels C and E will be discussed in the
section on metallography.   Incidentally, the reproducibility of data of
the two samples of steel A, independently heat-treated, should be noted.

Fig. 3 deals with a similar treatment to that discussed for Fig. 2,
except that the final operation subsequent to tempering was a slow
furnace cool instead of quenching in water.   Naturally a similar grouping
of the steels results from tempering below the eutectoid, although steel D
exhibits a peculiar hardness maximum at 680° C. (run 7).   Again the two
samples of A check very closely.   Above the critical point the increase in
hardness with temperature is approximately linear.

Fig. 4 illustrates the data obtained on a complete recheck of steel D,
which exhibited the anomalous high hardness at 680° C. on furnace-cool-
ing (run 7).   The check result on D has the same relation to A as it did
when it was water-quenched from the gradient furnace.   Both samples of
steel D correlate very closely above the eutectoid temperature, but from
about 580° to 720° C. there appears to be a real difference in reaction
to heat-treatment.

Fig. 5 shows the effect of water-quenching as compared with furnace-
cooling on steel B, typical of the first group, and on steel F, typical of the
second group, after tempering for 75 hr. subsequent to the quench at
1000° C.   While final water-quenching from below the critical, as com-
pared with furnace-cooling, results in slight increased hardness of both
steels, the difference is greater for steel F, particularly in the region of
maximum softening.   Above the critical, steel F fails to fully harden
on quenching.

In considering the surprising differences in the reaction to tempering
of these "similar" carbon steels, the question arises as to what role the
initial high-temperature quench may play in controlling or at least
affecting the differences recorded.

Fig. 6 illustrates the distribution of data obtained on gradient-tempering five of the steels after water-quenching from 1-hr. anneal at 850° C. The samples were allowed to cool slowly in the gradient furnace after tempering for 75 hr.   Comparison with Fig. 3 reveals that the curves are very similar to those obtained when the steels were water-quenched from 1000° C.   However, although the hardness maximum of steel D at 680° C. (Fig. 3) is absent from the 850° C. quench treatment (Fig. 6), the latter data correlate closely with those for the repeat run on steel D (Fig. 4), for the 1000° C. quench.   Above the critical, steel B exhibits the rapid rise in hardness that it showed following the 1000° C. treatment. Thus it may be stated that the reaction to tempering after quenching from 850° C. is practically identical to that obtained on quenching from 1000° C.

METALLOGRAPHIC STUDY OF THE ALLOYS

A complete metallographic study was conducted on all the bars discussed in this research, and a limited number of photomicrographs have been reproduced to illustrate the important characteristic reactions to tempering of steels typical of the two groupings already discussed.

The studies on steel B are representative of the microstructural features found in group I (steels B, C, E) and those on steel F are of the structures observed in group II (steels A, D, F).   The abnormal behavior of steel D at about 680° C. is also discussed and illustrated.

For metallographic preparation, the 12-in. long bars were cut transversely into several short sections and polished on the longitudinal machined surface on which the hardness determinations had been made. It was thus possible to correlate directly the microstructure with the various hardness determinations.   The samples were etched in 2 per cent picric acid in alcohol and the selected structures recorded at the highest useful magnification, 2000 diameters.   Reproductions of unetched sections, showing graphite, were made at 200 diameters magnification.

Figs. 7 to 12, from steel F, are typical structures found in steels tempered for 5 hr. after water-quenching from 1000° C.   The relation of the distribution of finely spheroidized carbide to both the coarse and fine martensite configuration is very clearly shown in Fig. 7 (490° C.).   The presence of resolved carbides in preferred directions within the large needle should be noticed.   This is the only record of this nature observed by the authors.   As the tempering temperature is raised some of the carbide spheres show progressive increase in size at the expense of other carbide particles that are obviously beyond resolution of the microscope. Evidence of the original acicular structure is found after 5 hr. at 715° C. (Fig. 11).   At 775° C. (Fig. 12) the appearance of pearlite with tendency to abnormality may be noted.

In Figs. 13 to 34 is presented a series of illustrations depicting the influence of tempering temperatures ranging from 470° to 775° C. on
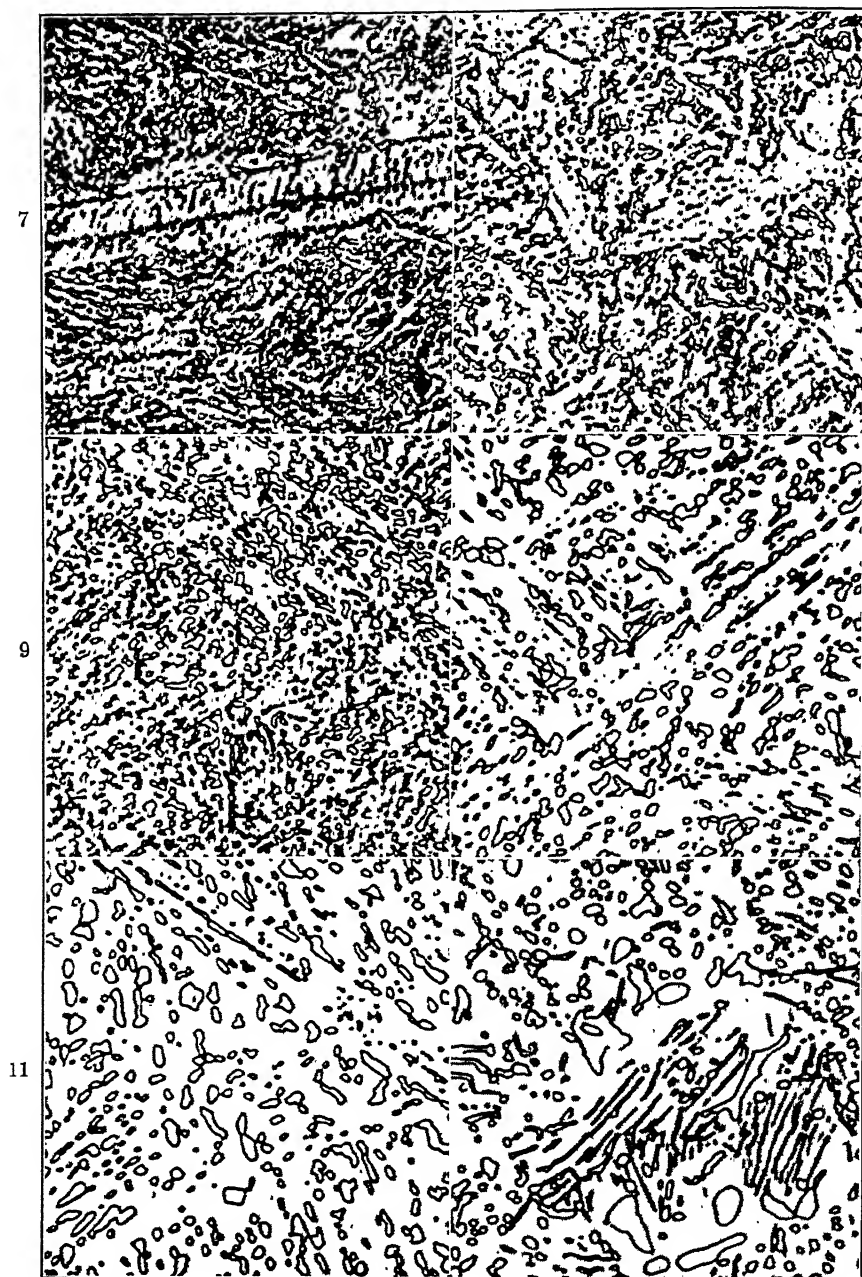
FIGS. 7–12.—STEEL F. CORRELATE WITH FIG. 1, RUN 4, SHOWING EFFECT OF
TEMPERING 5 HOURS AFTER WATER QUENCH FROM 1 HOUR AT 1000° C.   × 2000.
ETCHED IN 2 PER CENT PICRAL.
   Steel furnace-cooled in gradient furnace after tempering at: Fig. 7, 490° C.;
Fig. 8, 555° C.; Fig. 9, 620° C.; Fig. 10, 680° C.; Fig. 11, 715° C.; Fig. 12, 775° C.

FIGS. 13–22.—STEELS B (LEFT) AND F (RIGHT), TYPICAL OF GROUPS I AND II CORRELATE WITH FIG. 3 SHOWING EFFECT OF TEMPERING 75 HOURS AFTER WATER QUENCH FROM 1 HOUR AT 1000° C.   × 2000.   ETCHED IN 2 PER CENT PICRAL.

Steels furnace-cooled in gradient furnace after tempering at: Figs. 13 and 14, 470° C.; Figs. 15 and 16, 495° C.; Figs. 17 and 18, 525° C.; Figs. 19 and 20, 555° C.; Figs. 21 and 22, 605° C.
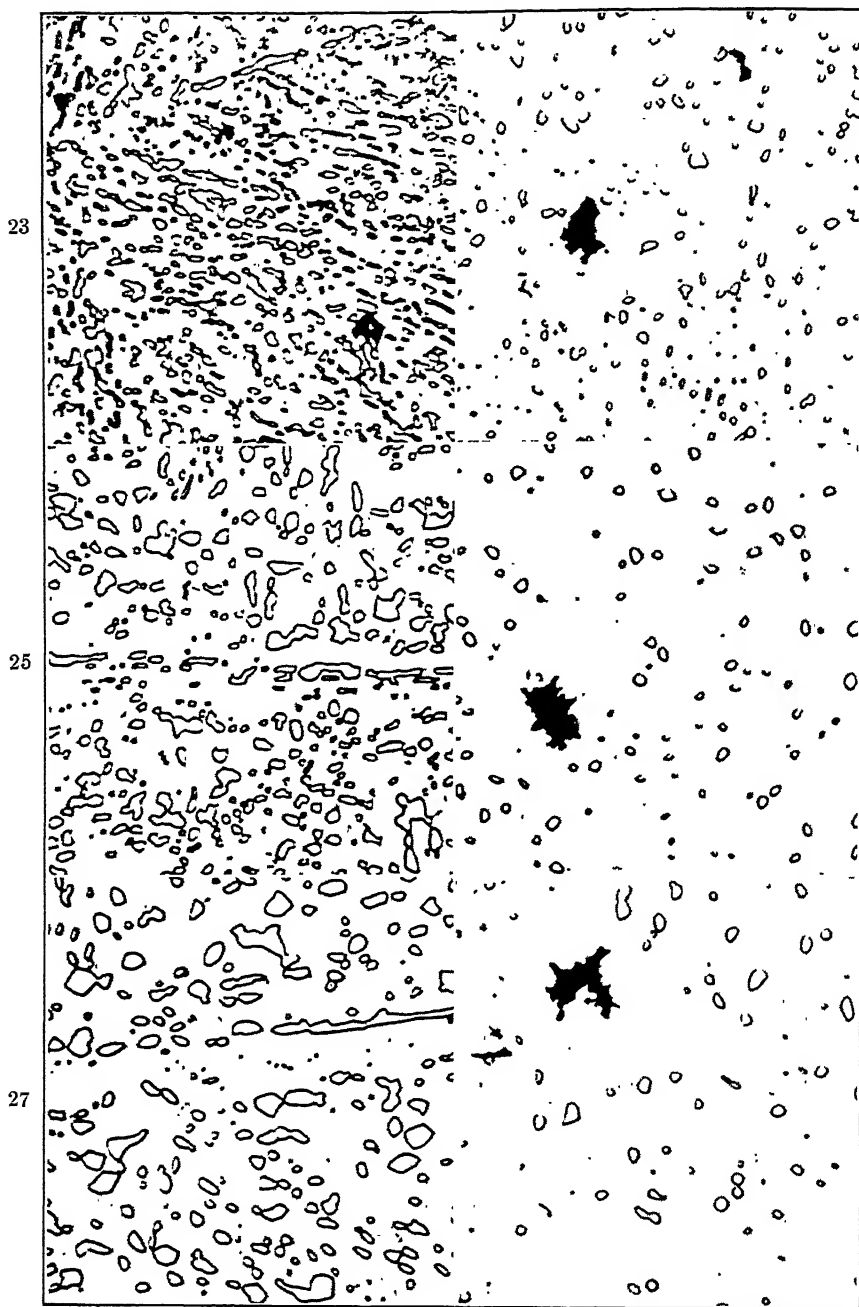
Figs. 23–28.—Steels B (left) and F (right) tempered 75 hours after water
   quench from 1 hour at 1000° C.   × 2000.   Etched in 2 per cent picral.   .
      Furnace-cooled after tempering at: Figs. 23 and 24, 620° C.; Figs. 25 and 26,
650° C.; Figs. 27 and 28, 680° C.

Figs. 29–34.—Steels B (left) and F (right) tempered 75 hours after water quench from 1 hour at 1000° C. × 2000. Etched in 2 per cent picral.
Furnace-cooled after tempering at: Figs. 29 and 30, 715° C.; Figs. 31 and 32, 745° C.; Figs. 33 and 34, 775° C.

the two groups of steels, as typified by steels B and F.   The alloys were quenched from 1000° C., tempered for 75 hr. and slowly cooled in the gradient furnace.   The microstructures should be correlated with the hardness data given in Fig. 3.

The tempering temperatures considered in Figs. 13 to 22 range from 470° to 585° C.   From 470° to 555° C., the progress of carbide coalesence is not markedly different in the two steels, but at 585° C., while spheroidization progresses, the amount of carbide in steel F appears to be diminishing.   Only slight indication of this phenomenon may be considered to be evident at 555° C., while the difference in behavior of the steels at this temperature is clearly revealed in the hardness data (Fig. 3).

In photomicrographs 23 to 28 the differences between steels B and F become increasingly evident as the tempering temperature increases from 620° through 650° to 680° C.   Indeed, the reason for the existence of maximum softness at 680° C. in steel F is at once apparent in the profound decrease in the amount of cementite particles.   Apparently even greater softening would have resulted except for the fact that the relatively few carbide particles still present maintain a general distribution of many particles rather than favor any appreciable increase in size.

In the previous research evidence was submitted to demonstrate that the decrease in amount of cementite was explained by the amount of graphitization.   The black areas in Figs. 24, 26 and 28 are graphitic carbon.

At 715° C. (Fig. 30), a rapid increase in the amount of cementite and in the particle size is evident in steel F.   At this temperature the hardness of steel F approaches that of steel B, the former being 10 Rockwell B numbers lower than the latter, whereas the difference was 18 units at 680° C.   The microstructural features of steel B when tempered below the eutectoid inversion are similar to those usually associated with the anticipated behavior of a high-carbon steel on tempering.

Above the eutectoid temperature (Figs. 31 to 34) the appearance of pearlite may be noted.   However, the abnormal structure taken from steel F on treating at 775° C., is particularly interesting.   This abnormal feature has previously been reported in this research after only 5 hr. tempering of steel F at 775° C. (Fig. 12).

Thus we have a striking suggestion of a correlation between abnormal reaction to tempering or graphitization and abnormality in the usually accepted sense of the term on heating above the critical, followed by slow cooling.

The fact that subcritical heat-treatment may result in a complete change in the constitution of a steel is well shown in the microstructures from steel F taken from unetched polished sections at 200 diameters (Figs. 35 to 42).   The amount of graphite progressively increases as the
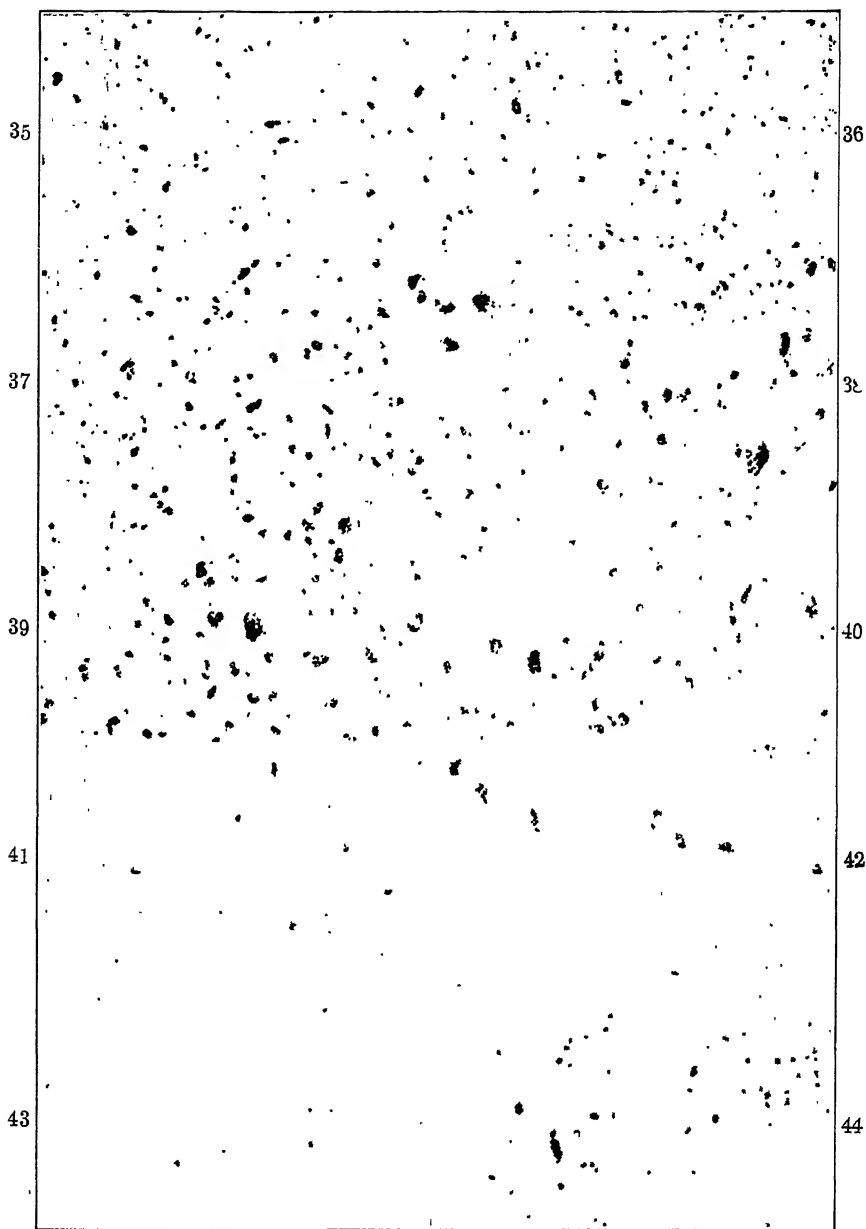
FIGS. 35–44.—STEELS F (FIGS. 35–42) AND B (FIGS. 43–44) TYPICAL OF GROUPS II
AND I. × 200. UNETCHED.

Correlate with Fig. 3 and with etched photomicrographs, Figs. 20, 22, 24, 26, 28, 30, 32, 34 and Figs. 19, 21, 23, 25, 27, 29, 31, 33, respectively. Steels furnace-cooled after tempering at: Fig. 35, 555° C.; Fig. 36, 585° C.; Fig. 37, 620° C.; Fig. 38, 650° C.; Fig. 39, 680° C.; Fig. 40, 715° C.; Fig. 41, 745° C.; Fig. 42, 775° C.; Fig. 43, 680° C (cf. Fig. 39); Fig. 44, 775° C. (cf. Fig. 42).

temperature of tempering is raised from 555° to 680° C., as may be forecast from the hardness data.   At 715° C., the quantity of graphite is less than that produced at 680° C., but it is still fairly plentiful.   It is apparent from Figs. 40 and 41 that the cementite is more stable just above the eutectoid (745° C.) than below it (715° C.).   At 775° C., there is some increase in graphitization.

The contrast in behavior of steel B is best shown by comparing the unetched structure observed at 680° C. (Fig. 43), with that of steel F at the same temperature (Fig. 39).   Below the eutectoid steel B appar-
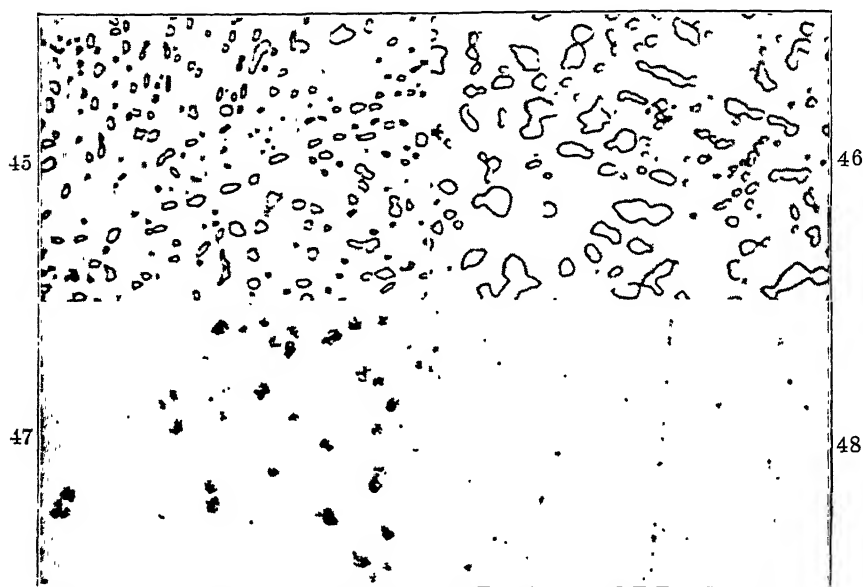
FIGS. 45–48.—STEEL D. EXHIBITING ABNORMAL BEHAVIOR ILLUSTRATED IN FIGS. 3 AND 4, RUN 7. TEMPERED 75 HOURS AND FURNACE-COOLED AFTER WATER QUENCH FROM 1 HOUR AT 1000° C. ETCHED CARBIDES, × 2000; GRAPHITE UNETCHED, × 200.

Figs. 45 and 47, tempered 650° C., Rockwell B82; Figs. 46, 48, tempered 680° C., Rockwell B92.

ently is not susceptible to graphitization, while above the eutectoid (Fig. 44) it is slightly more susceptible than steel F.

Figs. 45 to 48 are included for the purpose of correlating the abnormal hardness of steel D at 680° C. (Fig. 4) with the metallography of the sample.   The regular decrease in hardness up to 650° C. correlates with the disappearance of cementite due to dissociation and formation of graphite.   However, at 680° C., the sample appears to revert to the characteristic behavior of the first group of steels (steel B) where regular progress of spheroidization and little graphitization are observed. Indeed, the reversion, once initiated at 680° C., persists up to the eutectoid temperature.

The hardness data indicate that the hardening temperatures 850° and 1000° C. have little influence on the subsequent reaction to tempering of the two groups of steels. Microscopic examination confirms this similarity in behavior. However, when steel F was tempered at 550° C., the sample prequenched from 850° C. was about four hardness units softer than the one quenched from 1000° C.

A comparison of Fig. 53 (850° quench and temper) with Fig. 20 (1000° C. quench and temper) show that the lower hardness in the former was due to a greater degree of carbide coalescence. Some difference could be noted in the number and size of the graphite particles, although the total quantity appeared similar. They appeared to be more numerous and smaller after the 850° C. quench and temper.

A comparison of Figs. 49 and 50 (850° quench) with Figs. 43 and 44 (1000° C. quench) shows the relationship observed in steel B after tempering below (680° C.) and above (775° C.) the A_1 inversion, while the relation existing from steel F is similarly shown by comparing Figs. 51 and 52 with Figs. 39 and 42.

In most of the specimens examined under the microscope the graphite particles were distributed in a uniform manner. However, steel F, after the 850° C. quench and 75-hr. temper, showed evidence of a striation or lamination. This is illustrated in Fig. 54, at 80 diameters, for a section tempered at 620° C. The phenomenon may result from carbide segregation or may be accounted for by the presence of graphitizing element or elements in a segregated distribution.

Space permits only a brief reference to the typical tempered and quenched microstructures from groups 1 and 2 as indicated by records taken from steels B and F respectively.

Fig. 55 (steel F) is typical of the structure observed in both steels B and F when quenched from 1000° C. and tempered at 775° C. for 5 hr. and again water-quenched. The microstructure is essentially martensitic, although a few areas of very fine black pearlite (troostite) may be noted. The free carbide that has remained out of solution is fine and uniformly dispersed. After requenching subsequent to "tempering" for 75 hr. at 775° C., the structures of the two steels are quite dissimilar. Steel B (Fig. 56) is almost entirely martensitic while steel F (Fig. 57) is finely pearlitic (troostite). The hardness data show that steel B fully hardens to Rockwell C65, whereas steel F hardens only to Rockwell C40 (Fig. 2) as a result of the water quench.

The divergence in the behavior of these steels on quenching above the eutectoid merits further investigation.

DISCUSSION OF RESULTS

For many years it has been well known that steels of similar chemical composition may behave very differently when heat-treated under

strictly comparable conditions. However, these observations have related to differences in hardenability on quenching, and it is only within recent years that variation in "body" or "personality" of steels has been definitely correlated to some sound scientific principle—the phenomenon of reaction rates as a function of austenitic grain size.
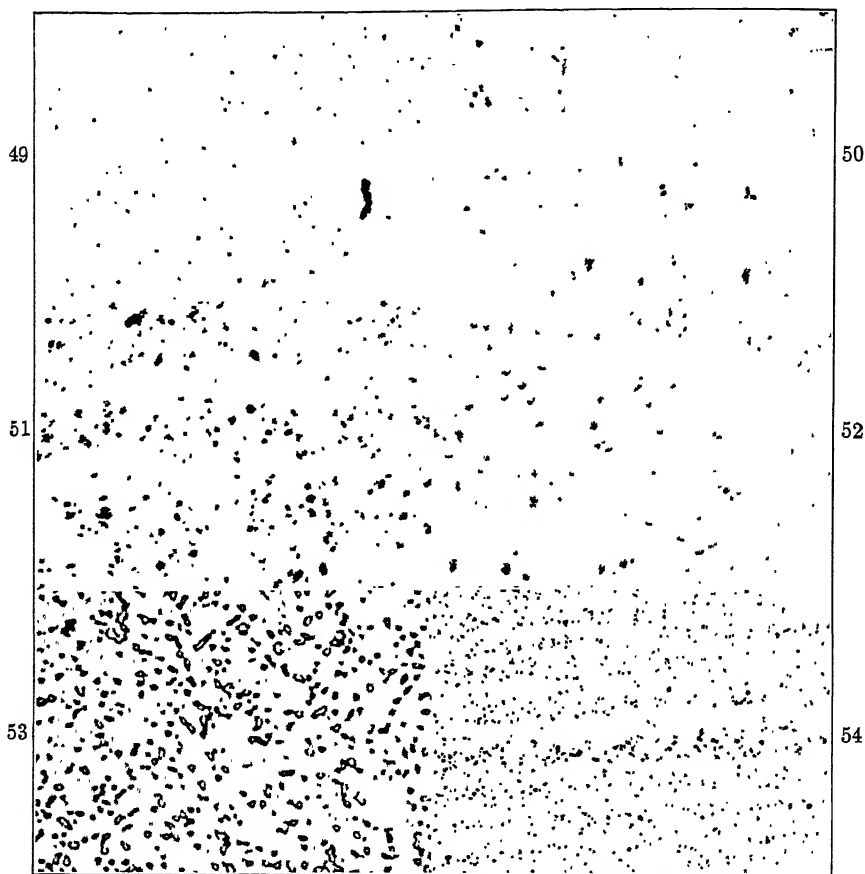
FIGS. 49–54.—STEELS B (FIGS. 49, 50) AND F (FIGS. 51–54).   TEMPERED 75 HOURS AND FURNACE-COOLED AFTER QUENCHING FROM 1 HOUR AT 850° C.
Figs. 49 and 51, tempered 680° C.; Figs. 50 and 52, tempered 775° C., unetched, × 200; Fig. 53, tempered 555° C., etched, × 2000; Fig. 54, tempered 620° C., unetched, × 80.

The work of the present authors clearly reveals that these differences may extend to the behavior on tempering the quenched steels, and to what may be termed the "rate of tempering," although a satisfactory unit of measurement is not as readily established as in studies on the decomposition of the austenite solid solution. Accordingly, it has been the chief concern in the presentation of this research to submit data relevant
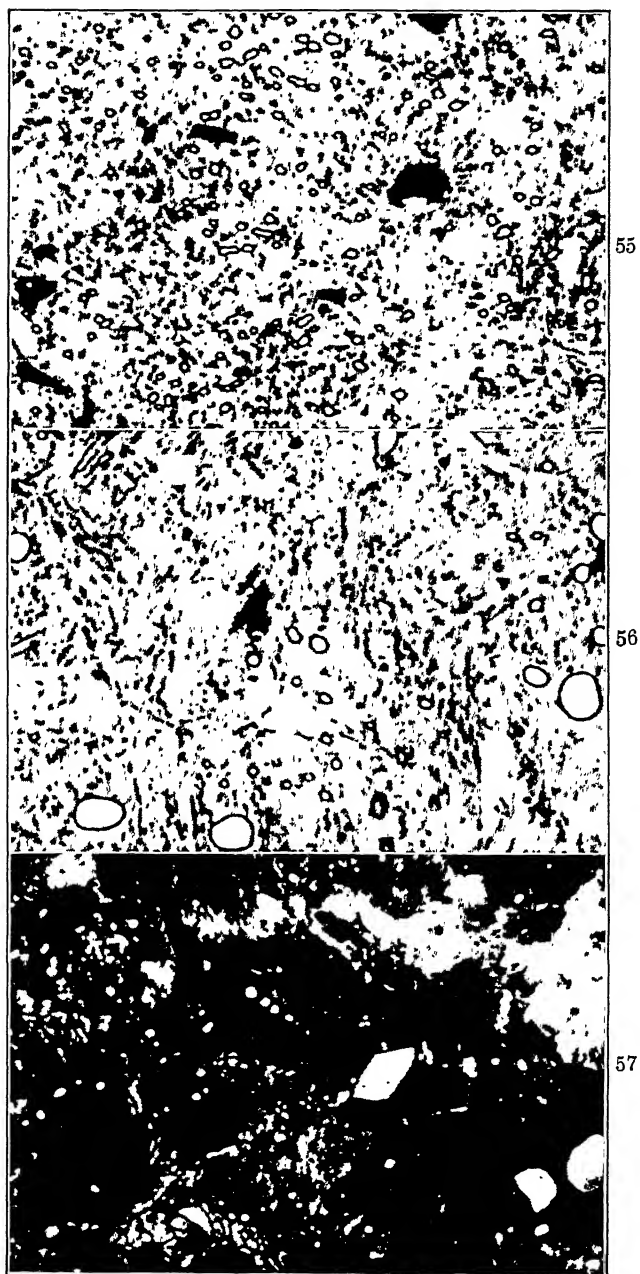
FIGS. 55–57.—STEELS B AND F, TEMPERED 75 HOURS AND WATER-QUENCHED AFTER INITIAL QUENCHING FROM 1 HOUR AT 1000° C.   × 2000.
Fig. 55, typical of B and F, tempered 775° C. for 5 hours, water-quench; Fig. 56 steel B, tempered 775° C. for 75 hours, water-quench; Fig. 57, steel F, tempered 775° C. for 75 hours, water-quench.

to the following points: (1) definite demonstration of the order of magnitude of the variation in reaction to tempering, as revealed by hardness measurements from 450° C. upward; (2) illustration of the nature of the structural changes accompanying the tempering operations by the use of photomicrography at maximum resolution; (3) consideration of reaction differences recorded.

Although the differences revealed relate essentially to prolonged tempering times, and occur at the higher tempering temperatures, it is suggested that apparent similarity at lower temperatures of treatment and for shorter periods is apparent rather than real, and that to render these variations manifest is merely a question of refinement of present-day experimental technique.

The following general conclusions can be drawn regarding the six hypereutectoid steels whose behavior on prolonged treatment divides them into two groups—B, C, E, and A, D, F—when tested at temperatures ranging from 500° to 800° C.:

1. In group II, steels A, D and F, minimum hardness is obtained at 680° C., some 50° C. below the eutectoid inversion, whereas in group I, steels B, C and E exhibit a minimum just below the eutectoid temperature.

2. The amount of cementite present in steels A, D and F reaches an apparent minimum at about 680° C., while it remains practically constant in steels B, C and E.

3. Graphitization is a maximum at 680° C. in A, D, F, and this accounts for the minimum in the amount of cementite revealed by the metallographic studies. Between 680° C. and the lower critical temperature the quantity of graphite decreases as the temperature increases. When the critical temperature is approximated the amount drops to a low value. It begins to increase immediately with further increase in temperature, although at the highest temperature tested, 800° C., it is still very much lower than the quantity present at 680° C. The group of steels that did not graphitize on tempering, B, C and E, exhibited slightly more graphitization on heat-treating above the critical than did steels A, D and F.

4. Steels that graphitize markedly at subcritical temperatures appear to form an abnormal microstructure when furnace-cooled after treatment above the lower critical.

5. The carbide present in martensitic needles appears to precipitate along certain preferred planes *within the needle* when the martensite is heated to the temperature of decomposition. It is considered that Fig. 7 demonstrates this feature in an unusually clear manner. However, in most of the observed cases, resolvable carbide particles do not appear in the needles, although there is usually a speckled appearance.

6. The variation in characteristics and grouping of the steels do not result from the high temperature of quench. Similar results obtain whether the steels are water-quenched from 850° or from 1000° C.

Undoubtedly the most remarkable feature observed in the research relates to the profound difference in the steels of the tendency to graphitization on prolonged tempering. In the previous research by the authors (reference 1) analyses for graphite content of the tempered bars were obtained by courtesy of Mr. A. C. Chamberlin, Bethlehem Steel Co. These data demonstrated that as much as 85 per cent of the cementite present in the A, D, F series of steels may decompose into graphite and iron. Although satisfactory analyses for graphite cannot be taken from a gradiently treated bar, there is little doubt that the maximum amount of graphitization in group II (typified by steel F, Fig. 28) exceeds 50 per cent.

An observation that merits more extensive investigation relates to the tentative correlation between graphitization at temperatures *below* the critical with the development of abnormal structural characteristics in the steel when slowly cooled from *above* the critical. Despite the large amount of research into the cause of abnormality, no agreement has been reached among metallurgists. However, it may be noted that the abnormal type of structure recorded in steel F is associated with high residual metallic aluminum. Steel F contains 0.025 metallic aluminum, whereas in steel B the aluminum content is nil. Both steels contain a little less than 0.01 per cent aluminum oxide. Additional data must be accumulated before any extended observations can be made.

A further observation to which attention should be drawn relates to the difference in the shape and distribution of the carbides as coalescence proceeds during tempering. The carbides lose the configuration associated with the original martensitic needles, and assume a spheroidal form most readily in the steels that exhibit the marked tendency to graphitize. A comparison of the structural differences in these two groups of steels in correlation with the softening characteristics of the steels is well shown in the composite diagram, Fig. 58, which is self-explanatory.

Finally, the question arises as to why steels of similar chemical analysis behave so differently on tempering. The redetermination of aluminum contents appears to afford some clue to the reason for the variation. Thus, steels A, D and F, which graphitize, all have high metallic aluminum—0.005, 0.011, and 0.025 per cent, respectively— whereas steels B, C and E, with the relatively stable carbides, have only 0.000, 0.005, and 0.000 per cent aluminum, respectively. However, it must be emphasized that the steels tested appear to be distinctly self-grouping, and do not exhibit a gradual transition in reaction from group I

FIG. 58.—CORRELATION BETWEEN HARDNESS AND MICROSTRUCTURE OF TWO HYPEREUTECTOID STEELS OF SIMILAR ANALYSIS BUT DISSIMILAR REACTION TO TEMPERING FOR 75 HOURS AFTER WATER-QUENCHING FROM 1000° C. Original magnification 2000; reduced approximately ¾ in reproduction.

STEEL	B	F
C	1.04	1.00
Mn	0.30	0.32
Si	0.44	0.27
Cr	0.05	0.06
Ni	0.06	0.16
Al	0.000	0.025
Al_2O_3	0.009	0.008

STEEL B

STEEL F

TEMPERING TEMPERATURE DEGREES CENTIGRADE

HARDNESS ROCKWELL B
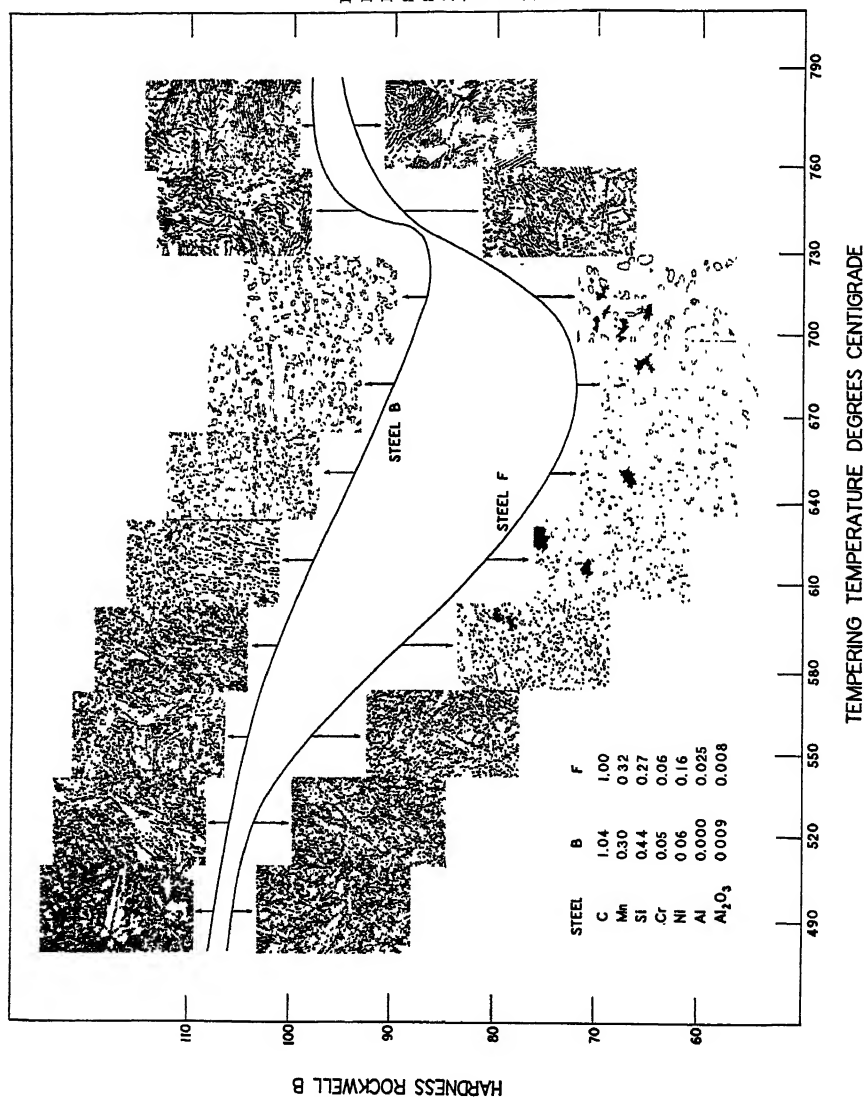
to group II.   Whether fortuitious or otherwise, each steel exhibits either a marked resistance to the formation of temper graphite or resists quite strongly the dissociation of the cementite.

In the initial selection of steels to be examined three open-hearth and three electric-furnace steels were chosen.   No correlation between mode of manufacture and reaction to tempering appears possible.   However, it is well known that silicon promotes graphitization whereas chromium acts as a strong inhibitor, even when present in only small amounts.   It is significant that steel B, with the highest silicon content (0.44 per cent), is one of the most stable alloys.   On the other hand, steel A, which belongs to the second group and is prone to graphitization, contains 0.12 per cent chromium, the highest value recorded for any of the steels.

Yield Point of Single Crystals of Iron under Static Loads

By M. Gensamer* and R. F. Mehl,† Members A.I.M.E.

THE stresses which initiate deformation processes in metals are fundamentally important in the study of the mechanical properties of metals. A point of inflection in the load-elongation curves obtained for single crystals[1] has been rather too readily interpreted as a true yield point, and the critical resolved shearing stress on the plane of slip taken as a material constant. Even early work showed that the stress at this point varies with rate of loading, but it has not been generally appreciated that creep tests under static loads alone are suited for determining the existence or nonexistence of a yield point.[2]

It has now been shown by Miller that single crystals of zinc[3] when loaded statically begin to yield at loads too small to measure; as a result there is no case now known, apart from that cited in the present paper, in which a true critical stress for yielding has been demonstrated for single crystals of metals.

The case of iron has especial interest: the existence of an upper and lower yield point and of an elongation at the yield point in ordinary iron and steel marks this substance as unusual, though the effects have been found to a very minor degree in other metals and alloys.‡ Most alloys do not show such marked phenomena when appreciable yielding begins, and accordingly modern practice is to speak of the yield strength of such materials, a stress read from the load-elongation curve after elongation has begun, rather than yield point. The special behavior of iron suggests that it is more likely that single crystals of iron should have a true yield point than other metals.

The study of the mechanical properties of metals and alloys requires a determination of the crystallographic mechanism of deformation, whether deformation proceeds by slip, twinning, or cleavage, or a combination of these, and a determination of the stresses that induce these modes of deformation. With this information, a study of the rates of work-

* Assistant Professor of Metallurgy and Member of the Staff of the Metals Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

† Director, Metals Research Laboratory and Head, Department of Metallurgy, Carnegie Institute of Technology, Pittsburgh, Pa.

[1] References are at the end of the paper.

‡ For example, Filma[4] finds a yield point in copper at −30° C., and G. Sachs and J. Weerts[5] in single crystals of gold-silver solid solutions.

hardening can proceed on a sound basis. The crystallographic mecha-
nisms of deformation in iron are now well understood,[6] but there is no
information on critical shearing stresses for slip and twinning and normal
stresses for cleavage obtained from experiments employing static loading.
The relative magnitudes of these quantities and their variation with rate
of loading must determine the type of deformation obtained under a given
set of conditions.[6]

The tensile curves on single crystals of iron obtained by Edwards and
Pfeil[7] were taken with finite loading rates, as were the yield points reported
by Fahrenhorst and Schmid.[8] The present paper records the first
results obtained in the present series of studies on the plasticity of iron
on static yielding stresses in single crystals of iron.

Experimental Procedure

The crystals used were manufactured by the strain-anneal method of
Edwards and Pfeil[9] with slight modifications.* No success was obtained
in applying this method to the purest available iron, and of necessity
decarburized mild steel similar to that used by Pfeil was selected. This
steel, before decarburization, had the following composition: 0.13 per cent
C, 0.36 per cent Mn, 0.010 per cent P, 0.025 per cent S, 0.09 per cent Si.

Bars $\frac{1}{2}$ in. in diameter were heated in nitrogen at 980° C. for two days,
cooled in the furnace to 750° C., held at this temperature over two weeks
in wet hydrogen, then cooled in the furnace to room temperature. The
decarburization in wet hydrogen reduced the carbon to the limit for
detection under the microscope. Following this treatment the bars were
strained between 2.75 and 3 per cent in tension, then gradually lowered
into a furnace, held at 880° C., in hydrogen. Large grains were produced,
many of which took up the entire cross section of the bar. The crystals
chosen for tensile testing were about $\frac{3}{4}$ in. long and nearly $\frac{1}{2}$ in.
in diameter.

The crystals tested contained a number of unavoidable minute
crystallites; the largest observed was 0.1 sq. mm. in area. No study has
yet been made of the number or size of these crystallites. The orientation
of each crystal was determined by back-reflection Laue photograms.
There was no evidence for linage structure; aside from the included
crystallites, the crystals appear to be quite free from imperfections.

The specimens machined from these crystals were about $\frac{1}{4}$ in. in
diameter. In some cases the fillets were outside the grain boundaries
and the extensometer used operated on a gauge length of $\frac{1}{2}$ in. entirely
within the grain boundaries. In all tests the knife-edges of the exten-
someter were at least $\frac{1}{8}$ in. away from the grain boundary, except with

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* The preparation of large crystals of iron by this method is much more difficult
than it appears to be. The results of considerable experience in this will be reported
in detail later.

the first crystal tested, which was only ⅝ in. long.   In the other crystals the reduced section, including the fillets, came wholly within the crystal; for these an extensometer of 2-in. gauge length was used, with the extensometer knife-edges on the specimen shoulders.   The purpose of the latter type of specimen was to eliminate the possibility that the observations might be affected by the presence of grain boundaries or indentations from the sharp extensometer knife-edges within the section of the specimen under maximum stress.   The fillet radius was not constant, but an effort was made to produce as gradual a transition from the reduced cylindrical section as possible.   The results obtained do not seem to have been influenced by the type of specimen used.   The machined specimens were carefully polished with metallographic polishing paper, examined for included crystallites, and then annealed at 850° C. either in hydrogen or in vacuum.   No oxidation during annealing was observed.   The crystals annealed in vacuum exhibited the same yield point behavior as those annealed in hydrogen; indeed, the vacuum treatment was performed in order to determine whether traces of residual hydrogen had exerted any special influence.

Axiality of loading was achieved through the use of modified Robertson shackles, in which the load is applied at the point of contact between a hardened steel plane and a steel ball located on the centroid of the specimen.   The modification consists of a device by which the holder into which the threaded specimen is screwed can be moved until the point of contact is accurately on the centroid of the specimen.   Upon the application of a load within the elastic range, adjustments were made until the extension of the specimen was the same to within one part in thirty at four points (90° apart) around the specimen.   This procedure thus constitutes a test for axiality of loading.   The extensometer was a Tuckerman optical strain gauge, with which an extension of two millionths of an inch can be detected; with a gauge length of ½ in., this corresponds to an extension of 4×10^{-6} in. per inch.

The specimens were loaded by dead weights applied in small increments, seldom over 200 lb. per sq. in. per increment, and frequently 100 lb. per sq. in. or less per increment.   The increments of load were added at intervals of time varying from about 6 hr. to 5 days.   Generally the load was increased when no creep was observed within about 8 hr.

The building in which the tests were made is exceptionally free from jars and vibration.   Nevertheless, the framework from which the specimen and its weights were supported was mounted on rubber pads.   It seems certain that dynamic stresses were very low.

RESULTS AND DISCUSSION

Nine crystals were tested in this way.   All of them exhibited a well defined yield point, which ranged from 3600 to 5200 lb. per sq. in.   The

range in yield point noted is probably associated with the orientations of the crystals studied. The slip system in iron[6] is so complicated, however, that yield points on a great number of crystals of different orientations would have to be determined before a correlation with orientation by means of shear stresses resolved on the many slip systems could be effected. No relationship was evident in the present studies.

This yield point, then, signifies the unit tensile stress below which no perceptible creep—i.e., creep of the order of 10^{-5} in. per inch under the conditions as described—could be observed, and above which perceptible creep could be readily observed. It seems hardly likely that longer
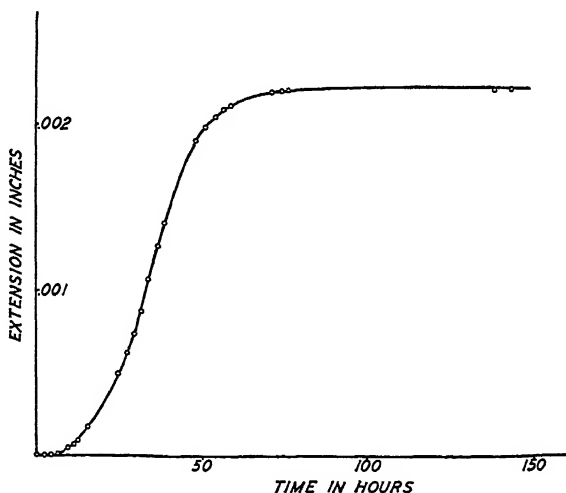
FIG. 1.—ELONGATION-TIME CURVE FOR SINGLE CRYSTAL OF IRON UNDER CONSTANT LOAD, AT A STRESS ABOVE THE YIELD POINT.

periods of observation below this point would have resulted in lower stresses for yielding.

The manner of yielding proved to be unexpectedly interesting. This may be illustrated by the elongation-time curve in Fig. 1, taken from one of the nine crystals studied; all of the other crystals tested behaved in a similar manner. The elongation did not begin immediately with application of load, or at least the elongation was very slow at first. The rate of elongation then increased and finally decreased to zero as the length assumed a steady state. One specimen was kept under observation for seven days after creep had ceased.

The rates of elongation at stresses above the yield point vary greatly. The rate is faster with greater increments of load than with smaller, but with approximately equal increments of load the same crystals exhibit different rates of creep (Fig. 2). The six curves shown in Fig. 2 are for creep at progressively higher loads taken in sequence; that is, curve 1 is for the first creep, curve 2 for creep at a higher load taken on the same

crystal after the creep at the lower load had ceased, and so on. It may be that this irregularity is a strain-aging effect.

It was expected that the form of the elongation-time curve would show an initially high rate, decreasing slowly as the crystal work-hardened. But the observed form is quite different and is surprisingly similar to reaction-rate curves for reactions in the solid state, such as the decomposition of austenite. The latter reaction proceeds by the formation of nuclei and the subsequent growth of these nuclei; could it be that these
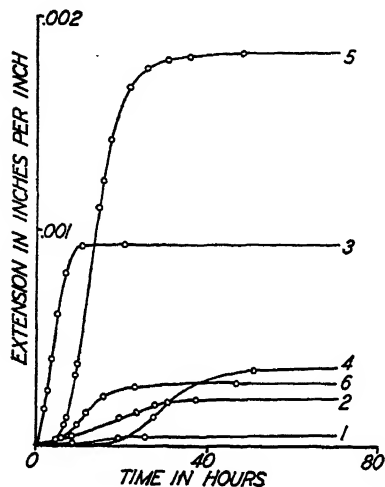
FIG. 2.   FIG. 3.

FIG. 2.—CONSTANT-LOAD EXTENSION-TIME CURVES FOR SINGLE CRYSTAL OF IRON, FOR A SEQUENCE OF LOADS AT STRESSES ABOVE THE YIELD POINT.

CURVE	INCREMENT OF STRESS, LB. PER SQ. IN.	STRESS, LB. PER SQ. IN.
1	248	4420
2	270	4690
3	273	4960
4	309	5270
5	318	5590
6	292	5890
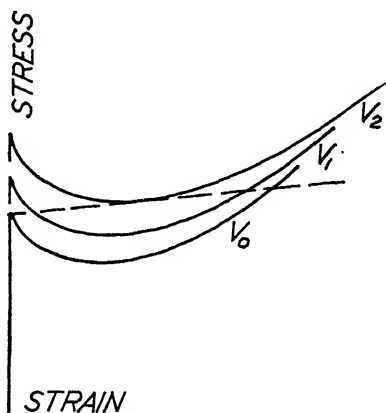
FIG. 3.—STRESS-STRAIN CURVES WHICH EXPLAIN SHAPE OF ELONGATION-TIME CURVES OF FIGS. 1 AND 2.

Curves marked V_0, V_1 and V_2 are stress-strain curves for increasing speed of testing. Dashed line is applied stress, which increases slightly as specimen extends and reduces in area. Flow will proceed at rate given by value of testing speed for each particular stress-strain curve crossed by this dashed line.

elongation-time curves represent the formation of strained regions increasing in size in a similar fashion? The cessation of elongation may be ascribed to strain-hardening, or perhaps to hardening through strain-aging, but the abnormally slow initial rate requires a special explanation. It seems most likely that the process is one in which a small amount of crystallographic translation produces stress concentrations which accelerate slip in regions already slipping, and that strain-hardening raises the yield point and diminishes the rate of flow at constant load until slip ceases.

It should be pointed out that curves such as those illustrated in Figs. 1 and 2 will always be found for materials exhibiting stress-strain curves showing a drop of the load on yielding when the test is carried out in the conventional testing machine. For illustration, consider the stress-strain curves of Fig. 3, which shows a family of curves for different speeds of testing. Three flow curves are drawn for testing speeds V_0, V_1 and V_2. At constant load, as in these single-crystal tests, flow proceeds from zero to a maximum rate and then back to zero rate. The stress is maintained at the value indicated by the dashed line, which shows a slight increase of stress with reducing area at constant applied load.[10,11]

The time rate of extension for any particular value of extension is given by the rate that is characteristic of the flow curve that intersects the dashed line at this value of the extension. Obviously, the time rate of extension will go from zero to a maximum and then back to zero only if there exists a dip in the flow curve such as is illustrated in Fig. 3.

SUMMARY

Static-load tests on nine single crystals of decarburized mild steel, in which elongation was measured with a sensitivity of 10^{-5} in. per inch, have shown the existence of a true yield point, a stress below which no perceptible permanent elongation occurs. At stresses at which yielding occurs the rate of elongation is initially low, then increases, and finally decreases to zero.

ACKNOWLEDGMENT

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DISCUSSION

(L. W. McKeehan presiding)

M. GENSAMER.—I want to call attention to Fig. 4, which is not mentioned in the paper. It is a stress-strain curve for one of our iron crystals, and is typical. The small figures beside the points on the curve are the number of hours the specimen was held at each load.

L. W. McKEEHAN,* New Haven, Conn.—There is, as all who have tried it know, great difficulty in obtaining large and perfect crystals of iron, and those who are interested in the properties of single crystals, not only of iron, have frequently been forced to the other solution of their dilemma; that is, to devise testing apparatus that
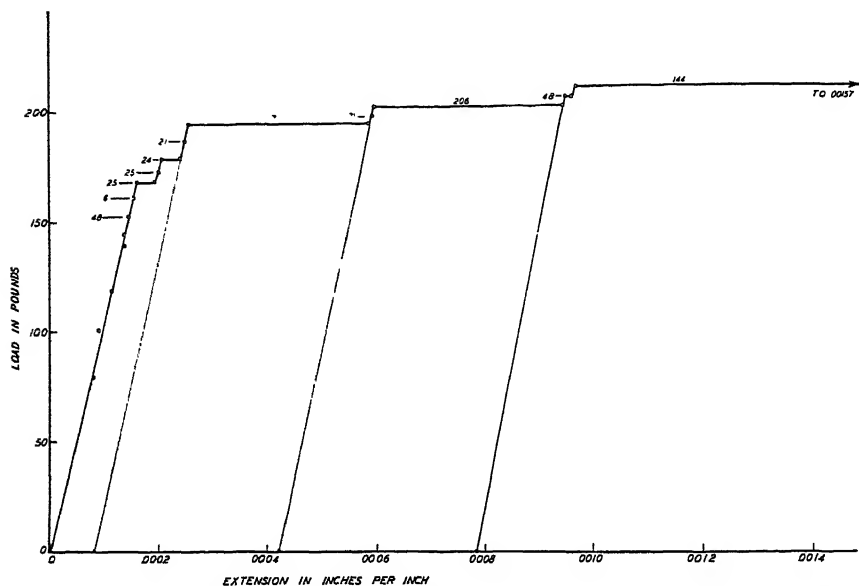
FIG. 4.—STRESS-STRAIN CURVE FOR A SINGLE CRYSTAL OF DECARBURIZED MILD STEEL.
Small figures beside curve indicate time of application of each load.

will handle small crystals as effectively as large, so that, denied the desirable 3-ft. crystal, they may operate on a 1-mm. crystal and get results of value. I cannot say that I have ever seen a very large crystal of iron that was entirely free from defects.

P. A. BECK,† Perth Amboy, N. J.—Has any effect of the orientation of the single crystals been found in this phenomenon of yield point? In cases where no deformation occurred within a few hours, might there be some deformation after, say, 1,000 or 10,000 hr.?

A. V. DeFOREST,‡ Cambridge, Mass.—Both this paper and the other one by Dr. Gensamer[12] are extremely important from the point of view of what we can learn

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* Director, Sloane Physics Laboratory, Yale University.
† Research Metallurgist, American Smelting and Refining Co.
‡ Associate Professor, Mechanical Engineering, Massachusetts Institute of Technology.
[12] M. Gensamer: The Yield Point in Metals. *Trans.* A.I.M.E. (1938) **128**, 104.

about strain-aging from stress-strain diagrams and yield-point phenomena. We know very little about the process and the various rates of strain-aging phenomena. As we go from single-crystal to polycrystalline material, perhaps there is a method of studying that will eliminate this mechanism of strain-aging which, after all, is the source of a large portion of the useful strength of our metals. The difficulty is that strain-aging is so common, and has been ignored for so long, that it is difficult to bring our minds to the place where every piece of steel that we see is a piece that has been strain-aged.

If we talk about strain-aging in an undeformed single crystal, it is difficult to get a level from which to start, but the further we go, the more understanding we will have of what constitutes the elastic strains in the space lattice before the strain-aging property has come into play.

Perhaps strain-aging is the only thing that gives us elasticity, anyway, and perhaps all materials that are not strain-aged are materials that are above a recrystallizing temperature.

F. M. WALTERS, JR.,* Youngstown, Ohio.—Did you observe the variations in Young's modulus with orientation, and will you give the figures on that? What type of extensometer did you use?

M. GENSAMER.—We have observed that the value we get for the yield point, and which may only be due to strain-aging, as Professor DeForest says, varies with different crystals. We have not yet tried to relate it to the orientation of crystals. I believe that the variation we get is less than we would expect from variation in orientation, because the crystals we have studied have been quite different in orientation.

As to the time below the yield point, while we did not hold at the load just below the yield point anything like 1000 hr., we held at that load plus some hours at a load a little below that, plus some hours at a load a little below *that*, and so on. The higher the load, the greater the effect ought to be, so that I am pretty sure there is some load at which we would observe no creep even if we held a full 1000 hours.

I can only agree with everything Professor DeForest has said, and would like also to emphasize the importance of strain-aging.

We observed a considerable variation in Young's modulus with these different crystals, but we have not tabulated it. I do not think we have studied enough crystals to get a good study such as has been made by Goens and Schmidt, and by a Japanese investigator using other methods.

F. M. WALTERS, JR.—Did you check the magnitude?

M. GENSAMER.—Yes. It varied from 20 to 40 million. The extensometer we used was a Tuckerman optical strain gauge on a gauge length of ½ in., with a sensitivity of roughly 10^{-5}.

A. A. SMITH, JR.† AND P. A. BECK,† Perth Amboy, N. J. (written discussion).—As early as 1934, Dr. Mehl emphasized the importance of creep tests in establishing yield points of single crystals. The interesting results of the present study of the yield point of iron single crystals show the fruitfulness of this idea.

The existence of a well marked induction period, and of a stepped creep curve seems to us to have a deep fundamental significance. Induction period, with no deformation at all, followed by sudden elongation (*Sprunghafte Dehnung*) has been

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* Research Engineer, Youngstown Sheet and Tube Co.
† Central Research Laboratory, American Smelting and Refining Co.

found also with single crystals of zinc.[13]   According to Orowan,[14] the occurrence of a slip is determined by the simultaneous effect of local stress concentrations due to flaws in the crystal, and of thermal agitation.   A slip starts when, at a certain moment, the locally concentrated stress happens to be sufficiently further increased by the haphazard thermal stress fluctuations in the lattice to overcome its relatively high inherent slip resistance.   The induction period can then be interpreted as the waiting time for such a chance thermal process to occur.

The higher the applied stress, the smaller becomes the stress increment that has to be put up momentarily by thermal fluctuation.   The probability of the slip process being thus larger for higher stresses, the average waiting time or "induction period" is shorter.   All factors that increase the number, or the stress-concentrating effectiveness of the flaws, or that amplify the thermal agitation of the atoms, will tend, according to this picture, to decrease the average waiting time.   The latter may
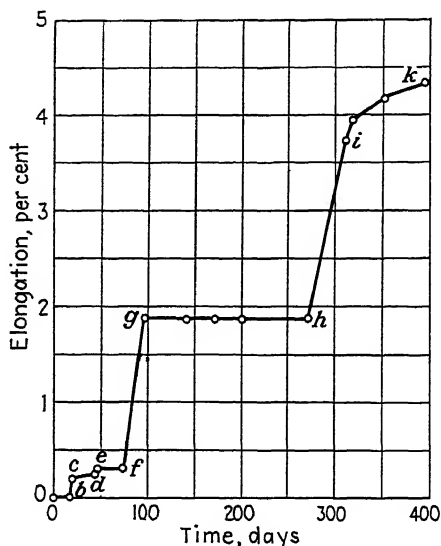
FIG. 5.—CREEP CURVE OF A HIGH-PURITY LEAD SPECIMEN AT 30° C.   STRESS 188 LB. PER SQUARE INCH.

become so small as to escape attention entirely; the creep curve then appears smooth. It seems very likely that dissolved foreign atoms in the lattice, as well as increased testing temperature, may produce such decrease.   With impure materials and higher temperatures discontinuous creep will therefore tend to disappear; on the other hand, the steps in the creep curves may be expected to be larger if very pure materials and lower testing temperatures are used.

Reference should be made in this connection to the careful study by Miller and Milligan,[15] showing that in the constant rate of loading type of test the yield point elongation of aluminum single crystals is more marked the lower the temperature and the purer the metal.   This is in agreement with the above views, if we consider that

[13] E. Orowan: *Ztsch. Physik* (1934) **89**, 634.

[14] E. Orowan: *Ztsch. Physik* (1935) **97**, 573.

[15] R. F. Miller and W. E. Milligan: Influence of Temperature on Elastic Limit of Single Crystals of Aluminum, Silver and Zinc.   *Trans.* A.I.M.E. (1937) **124**, 229.

in this type of testing the load continues to increase during the induction period, and that the extent of the following elongation will thus necessarily increase with the length of the induction period. We believe that this is a more probable explanation than that tentatively given by Miller and Milligan—namely, that "at low temperatures the glide planes have less tendency to rumple." This latter explanation seems to be in disagreement with the general experience that the rate of strain-hardening increases with decreasing temperature. It is interesting to note that according to Miller and Milligan the further deformation of the aluminum and zinc single crystals took place in a discontinuous fashion, even though the steps were small.

In this laboratory many creep tests have been carried out on polycrystalline lead and lead alloys. Many creep curves have been obtained that show a characteristically stepped form. Fig. 5 gives such a creep curve for high-purity lead (99.999 per cent Pb). The material was coarse grained; the cross section of the specimen was filled out by about four crystals. The probable error of the measurements was ±0.005 per cent; that is, in a much smaller order of magnitude than the sudden elongations corresponding to sections b-c, f-g and h-i of the curve. The number of careful measurements made on section g-h of the curve convinces us that there has been no elongation, exceeding the limit of our accuracy, during this period of 174 days. The initial induction period o-b was 18 days in this particular test.

Considering the high purity of the lead used, we believe that, at least in this case, the hypothesis of strain-aging should be definitely excluded from the explanation. The exceedingly frequent occurrence of the stepped creep curves, especially with high-purity lead, seems to indicate that this is a fundamental phenomenon of plastic deformation, as it should be according to the theory of Orowan. Another point in favor of the latter theory is the very large difference between the lengths of individual induction periods with the same material, and even in the course of one single creep test. These wide variations, which make stepped creep curves so hard to compare with each other, give rather the impression of a process involving chance than of a process, like aging or overaging, that would require a definite induction period. Orowan has described the deformation of a crystal as an "autocatalytic" process.[16] Once a "deformation nucleus" is formed—e.g., slip starts at a certain place—the deformation continues until the strain-hardening becomes large enough to stop it.

It might be interesting to continue the tests longer than 7 days after the first yielding has occurred, in order to find out whether or not further yielding results (as at points d, f and h on Fig. 5).

R. W. E. LEITER,* AND J. WINLOCK,* Philadelphia, Pa. (written discussion).— The work by Pfeil on iron single crystals, to which the authors refer, shows no well defined yield point or yield-point elongation in the conventional testing machine. However, on page 377 the authors say that "curves such as those illustrated in Figs. 1 and 2 will always be found for materials exhibiting stress-strain curves showing a drop of the load on yielding when the test is carried out in the conventional testing machine." How do the authors reconcile their deduction with the findings of Pfiel?

We have studied the six curves in Fig. 2 and we notice that with approximately the same stress increase curve 3 shows no induction period, curve 4 shows a very long induction period and curve 5 shows a very short period. There are also marked differences in rate and amount of extension. In the discussion, the authors mention this irregularity and suggest that it may be a strain-aging effect. Were there any marked differences in elapsed time after deformation stopped and before the subse-

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[16] International Conference on Physics, London, October 1934.

* Research Metallurgist and Chief Metallurgist, respectively, Edward G. Budd Mfg. Co.

quent load increments were placed on the specimens, which could explain the differences in curves 3, 4 and 5? In other words, we are very much interested as to whether in the author's opinion aging causes a return of the induction period just as aging of cold-worked polycrystalline iron causes a return of the yield-point elongation.

R. F. MILLER,* Kearny, N. J. (written discussion).—In 1934, Dr. Mehl said: "The proper way to attack the problem (of true yield points) would be to perform static loading or creep tests. A true yield point would be shown by a low stress level below which no yielding took place. Such an experiment on well formed large single crystals with close attention to axiality of loading would furnish valuable information." (Reference 2.)

Following his suggestion, while at the Hammond Laboratory, Yale University, I attempted to determine the yield point of pure zinc single crystals (reference 3). Much work had been done by Schmid and others on "the law of critical shearing stress," and it seemed that an exact determination of this critical stress would be worth while. After construction of a microscope extensometer that was accurate to $\pm 3.3 \times 10^{-6}$ in. per inch when used on a specimen having a gauge length of 6 in., creep tests disclosed that zinc single crystals had no critical shearing stress; they flowed under their own weight. However, these creep tests on zinc could not be interpreted to mean that the yield point was absent in all pure metallic single crystals, since the zinc had been tested only above its recrystallization temperature. Much evidence had accumulated to show that, at least in polycrystalline metals, flow was rapid above the recrystallization temperature, but very slow or absent below this temperature. For this reason, creep tests on zinc were abandoned, and single crystals of aluminum were examined.[15] It was unfortunate that owing to lack of time creep tests could not be used, and slow tensile tests had to be substituted. The results of the tests may not be as conclusive as though creep tests had been employed, but it was plainly evident that the yield point dropped sharply at the recrystallization temperature. It is significant that the recrystallization temperature was determined from polycrystalline aluminum, and that this temperature was evidenced in the single crystals as the temperature at which the yield points dropped sharply.

It would therefore be of great interest to know what effect temperature would have on the yield point of iron single crystals. If it could be shown that the yield point disappeared at about the lowest temperature of recrystallization of polycrystalline iron, a fundamental connection between the two phenomena would be demonstrated. Such information would be of value in the study of the creep strength of steel.

In regard to the remarks of Messrs. Smith and Beck, I would like to call attention to the fact that not alone was the yield-point elongation of the aluminum single crystals more marked the lower the temperature and the purer the metal, but also the yield point increased with increasing temperature, up to the recrystallization temperature. Thus, the extent of the yield-point elongation was less the longer the induction period, rather than the reverse, which they suggested.

The aluminum single crystals were extended in tension by adding a dead load at the rate of 3 lb. per minute. The yield-point elongation shown by this type of test would probably correspond to a drop of the beam if the test had been made with a conventional screw-type machine. If the tests on aluminum single crystals had been made in creep it is probable that they would have shown the same type of stepped creep curves as those shown in the present paper.

In creep tests on steel, an elastic extension is noted when the load is applied. When the creep test is finished and the load removed, elastic recovery takes place immediately in an amount approximately equal to that first noted on applying the

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* Research Laboratory, U. S. Steel Corporation.

load. This is true even though the steel has extended plastically several per cent during the test. It is thus evident that a material still has elastic properties even though it is being deformed in the plastic range. I should like to ask the authors what they consider to be the relationship between the yield point and the elastic limit.

P. A. BECK (written discussion).—Dr. Miller suggests that the joint increase in yield point and decrease in yield-point elongation found by Miller and Milligan is incompatible with the point of view previously submitted. I will now attempt to show that if the terms used are somewhat more sharply defined, such incompatibility does not actually appear.

Accepting the individual yield process as one involving chance, we cannot expect the individual induction period to have more than ephemeral significance. Significant would be, according to this point of view, the *average* induction period for any given load, taken from a large number of creep tests. This statistical interpretation of the induction period leaves us with the average induction period as a function of the stress.
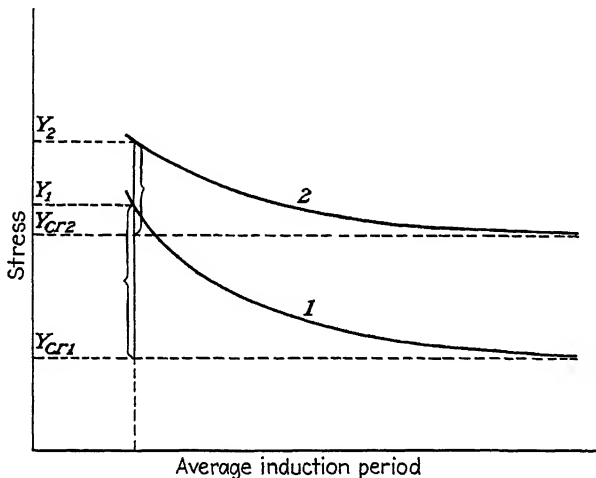
FIG. 6.

In decreasing the stress, the average induction period will increase. Should there exist a definite yield point, as determined by the complete absence of creep, it would mean that while the average induction period increases to infinity the stress tends asymptotically toward a finite value. These conditions are schematically represented in Fig. 6 by curves 1 and 2. Points Y_{cr1} and Y_{cr2} denote the corresponding yield points, determined by creep tests, at which the average induction periods become infinitely long. However, the following considerations do not depend on the existence or nonexistence of such absolute yield points. We may define Y_{cr} as the stress value at which the average induction period becomes very large for all practical purposes. It is evident, that, according to this picture, the constant rate of loading type of test, or the constant rate of straining type of test will not give any strictly reproducible "yield point."[17] For any given rate of loading there will be an average "yield point," derived from a large number of tests. This is a stress value at which

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[17] See the discussion of Winlock and Leiter's paper [*Trans.* Amer. Soc. Metals (1937) **25**, 176] in which it is stated that the upper yield point of fine-grained, low-carbon steel appears "void of reason" and "evasive," its exact location difficult.

the average induction period is sufficiently small to allow the yielding process to occur before the stress measurably further increases. Such average "yield points" (Y_1 and Y_2) will be higher than the corresponding yield points determined by creep tests (Y_{cr1} and Y_{cr2}), and the difference $Y - Y_{cr}$ will increase with the rate of loading.

We may expect the yield-point elongation to be larger the higher the stress Y_1 at which actual yielding occurs, as compared to Y_{cr}, the minimum stress at which creep may proceed with any probability. Actually, Winlock and Leiter find that both the yield point and the yield-point elongation of low-carbon steels are increasing with the rate of loading.

It should be appreciated, however, that yield point and yield-point elongation are not necessarily thus linked with each other. The yield-point elongation does not at all directly depend on the yield-point stress Y—it should rather depend on the *difference* $Y - Y_{cr}$. In order to illustrate this point, the curves in the figure have been so chosen that at temperature t_2, corresponding to curve 2, the average "yield point," at a certain rate of loading Y_2 is higher than Y_1 at temperature t_1, for the same rate of loading. The difference $Y_2 - Y_{cr2}$ is, however, smaller than the difference $Y_1 - Y_{cr1}$, so that the average yield-point elongation at temperature t_2 is smaller than the average yield-point elongation at t_1. Thus, here a *higher* yield point corresponds to a *smaller* yield-point elongation.

M. GENSAMER AND R. F. MEHL (written discussion).—The comments of Messrs. Smith and Beck are interesting and pertinent. Needless to say, we have considered thermal fluctuations as a possible cause of the induction-period effect. The length of the induction period (several hours) led us to take the simpler point of view expressed in the paper. We believe that Orowan's ideas can be used in an explanation of the lowered resistance to deformation (after deformation has begun), which is required by our explanation of the induction period, but while we hold Orowan's dynamic theory in the highest regard, we are not yet willing to abandon other points of view.

Messrs. Leiter and Winlock misinterpret our remarks. We did not wish to imply that a material for which the yield point has escaped detection in the conventional testing machine will necessarily *not* show an induction period in a dead-weight test. A material that *does* show a drop in the beam in conventional testing *will* show an induction period in dead-weight testing. We have not been able to correlate the differences between the curves mentioned with the elapsed time before the next load was applied. We are working on the effect of aging on stress-strain curves and hope to have more to say about this in the near future.

Dr. Miller's question concerning the relation between the yield point and the elastic limit may be answered by pointing out that any stress is an elastic stress (there is an elastic reaction to every applied load), and that elastic stresses above the conventional elastic limit are commonplace.

The Problem of the Temperature Coefficient of Tensile Creep Rate

By J. J. Kanter,* Member A.I.M.E.

Creep investigators have made extensive studies to determine the interrelation of stress, temperature and the tensile creep rates of metals. It has been suggested that at small stresses the secondary or constant creep rates obey a simple viscous law. Building upon this suggestion, departure from pure viscosity as stress increases may be expressed mathematically as a consequence of reversibly altered viscosity or "flowability" in the same sense that temperature change reversibly alters viscosity. From the index to alteration of viscosity, a value for the energy of secondary creep may be derived having the magnitude of the free energy of vaporized metal. The suggestion is made that application of stress alters the energy of secondary creep. Strain energy is argued to be but a minor factor in the energetics of secondary creep. A deformation mechanism involving the large energy associated with secondary creep implies a sort of solid self-diffusion process. Evidence indicates that creep strain above the recrystallization temperature takes place by crystallographically directed self-diffusion at grain boundaries and points of crystal defects. A self-diffusion theory of secondary creep is proposed, embracing the principles of the Dushman-Langmuir theory of solid diffusion. An equation is suggested whereby the rate of tensile creep may be related directly to the physical and structural character of the solid metal.

Basis of Investigation

Much of the investigation that has been given to the creep characteristics of metals and alloys has been directed toward studying the dependence of creep rate upon stress. Great interest has centered upon the approximately uniform rate of flow that has been demonstrated for numerous metals and alloys. At temperatures above the strain-hardening ranges of materials, this uniform rate frequently is attained after a relatively short period of initial rapid flow, and the period during which it persists determines for most practical purposes the useful life of the

material. Inasmuch as this period of uniform flow continues for many thousands of hours if stresses that confine creep rates within engineering limits are employed, creep stresses usually are defined in terms of the constant creep rate, although such creep stresses admittedly are inadequate for application to the more precise creep-design problems.

Some investigators believe that uniform creep rate is attained after sufficient deformation has occurred to bring about stress homogenization. Such a conception implies that the application of stress to a previously unstressed solid brings about a spontaneous series of slip action whereby adaptation to a new balance of forces is sought out. Similarly, as the primary creep is attributed to an adaptation upon stress application, creep recovery also results as a matter of adaptation to stress removal. Granting this conception for the approach to constant creep rate, this constant or secondary rate might then be considered as a consequence of the equilibrium attaining between stress cohesional forces. Discussion of the constant or secondary creep rate versus a stress function, from the point of view that it has this definite physical significance, may well be justified. The aim of this paper, therefore, is to point out some of the possibilities of interpreting this aspect of the secondary creep of polycrystalline metals in relation to the combined effects of temperature and stress upon the energy involved.

KEY TO NOTATION

v Constant tensile creep rate, in. per in. per hr.

σ Tensile stress, lb. per sq. in.

σ_0 Cohesive force, lb. per sq. in.

ϕ Flowability $= v/\sigma$.

ϕ_T Flowability constant at temperature T.

ϕ_0 Flowability constant at $T = 0$.

T Absolute temperature, deg. Kelvin.

Q Quantity of energy, cal. per gram atom.

R Gas constant $= 1.987$ cal. per deg. mol.

ln   Natural logarithm.

W Strain energy.

E Young's modulus of elasticity.

$f(\sigma)$ Exponential stress function for creep rate.

ΔS Change in entropy.

Δ^*S Alteration in energy of secondary creep due to stress.

j Mechanical equivalent of heat $= 4.185 \times 10^7$ erg per calorie.

N_0 Avogadro's number $= 6.061 \times 10^{23}$ atoms per gram atom.

h Planck's constant of action, 6.554×10^{-27} erg seconds.

δ Interatomic distance, Ångstroms or centimeters.

λ Points of dislocation per centimeter.

Viscous Creep

Assuming that the reader is familiar with the character of creep-time curves,[1] the derivation of secondary creep rates, and the various schemes whereby creep stresses are deduced, the question of *viscous creep* at small stresses is submitted for further consideration. The idea of interpreting metallic creep as a departure from pure viscous flow has been reviewed by the writer[1] and discussion by Nadai, Norton, and Moore and Betty developed a considerable justification for such a theory. "Pure viscous flow" here means deformation at constant temperature in accordance with the equation:

$$v = \phi\sigma \qquad [1]$$

where v is the constant rate of straining, σ is the stress, ϕ is a constant having the dimensions of fluidity or reciprocal viscosity. While, strictly speaking, this constant should be defined for an instant of strain, for the present purpose, where only the constant creep rate at constant stress is being considered, ϕ is defined as sensibly unchanging for the duration of secondary period of creep. The validity of the "pure viscous" creep idea for small stresses is strikingly demonstrated by the Moore and Betty tests on lead and lead alloys. (See discussion to ref. 1.) The trends of log-log plots of steel data, however, had previously suggested that such a relationship might be valid for extrapolating creep rates to stresses below the experimental range.

Extension of the validity of equation 1 to higher ranges of stress requires that the fluidity factor ϕ be treated as a function of stress. By plotting the quotient v/σ as a function of the stress σ, a value ϕ_T is obtained by extrapolating to the ordinate. This value ϕ_T is what might be termed the "flowability" of the material as stress approaches zero. Such a diagram is shown in Fig. 1a, where the logarithm of ϕ is plotted against a root of σ and shows the relationship at various temperatures for tests on a mild steel reported by Kanter and Spring.[19] The succeedingly higher values of ϕ_T with increase of temperature establishes this constant as a function of temperature. In some series of tests, $\log (v/\sigma)$ appears as a sensibly linear function of stress σ, which condition may be expressed by the equation,

$$v = \phi_T\sigma e^{\alpha\sigma} \qquad [2]$$

in which pure viscosity is implied for $\sigma = 0$. The flowability may thus be considered as increasing in geometrical proportion to the stress,

$$\phi = \phi_T e^{\alpha\sigma} \qquad [3]$$

The linear relationship between $\ln (v/\sigma)$ and σ, however, does not hold in general and extrapolations to ϕ_T are better made by replacing $\alpha\sigma$ with

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[1] References are at the end of the paper.

a more suitable function giving a linear plot as illustrated in Fig. 1a. Generalizing equations 2 and 3,

$$\ln \left(\frac{v}{\phi_T \sigma} \right) = f(\sigma) \tag{4}$$

$$\ln \left(\frac{\phi}{\phi_T} \right) = f(\sigma) \tag{5}$$

Equations 2 and 4 express an isothermal dependence of creep rate upon stress. Fig. 1a indicates that the constant ϕ_T varies with temperature.
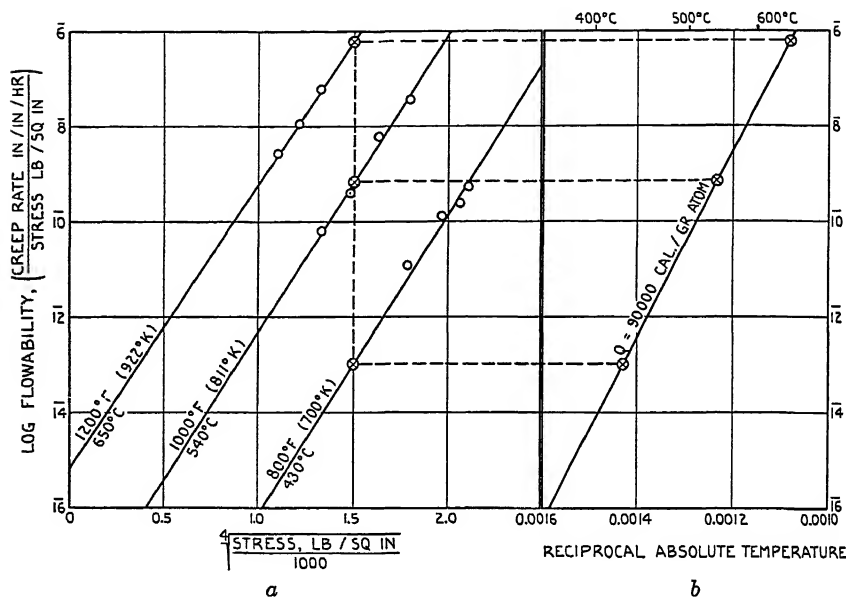
FIG. 1.—"FLOWABILITY" OF 0.17 PER CENT CARBON OPEN-HEARTH WROUGHT STEEL.
a. As a function of stress.   b. As a function of absolute temperature.
Kanter and Spring data.[19]

As temperature rises ϕ_T assumes successively higher values, while the slope that determines $f(\sigma)$ undergoes but little change.

SECONDARY CREEP ENERGY

If the flowability of metals as defined by ϕ be considered as a thermodynamic function, its relationship to the reciprocal of the absolute temperature $(1/T)$ assumes a significance akin to the fugacity, a quantity defined by G. N. Lewis[2] to express the activation of atoms and molecules. Dushman[3] introduced a similar idea in discussing the exponential relation between temperature and various other properties of solids by drawing an analogy to the laws governing the rates of physical and chemical reac-

tions. It has been shown that the viscosity of glass as plotted against the reciprocal of the thermodynamic temperature scale determines a straight line from whose slope may be computed the energy required to overcome the cohesive forces associated with glass molecules. Data for the relative efflux of tin and lead through small orifices at various temperatures was treated by Dushman on the same basis. Carrying the analogy further, Dushman contends that the measurement of the strength of metals above the equicohesive temperature involves the fluidities of the metals in such a manner as to justify the use of relative strength in determining an equilibrium constant. From such calculations, Dushman obtains energy values for various metals greater than the heat of fusion and considerably less than the heat of evaporation. The conclusion that he draws from the strength data is that the type of reaction associated with plastic flow of metal is similar to that which occurs in the fusion of metal, the energy involved being the amount required to cause a translational motion of atoms. The various kinds of viscosity data, however, showed the temperature coefficient to involve somewhat higher energies than those associated with the effects of temperature on strength.

Following the foregoing line of reasoning, the results of creep tests are likewise amenable to an energy analysis. The temperature coefficient of the flowability constant ϕ_T may be studied by determining a set of relative values along a stress ordinate in Fig. 1 and plotting them versus the corresponding values of reciprocal absolute temperature, as illustrated in Fig. 1b. From the slope of this plot, then, is determined a value that may be considered as an index to the energy involved in the pure viscous flow of metal under small stresses. Writing this relationship in the form of an equation, where the energy approximation is expressed as the quantity of heat in calories per gram atom of metal, Q, involves the gas constant R (1.987 cal. per deg. mol.) and ϕ_0, the flowability at $T = 0$,

$$\ln\left(\frac{\phi_T}{\phi_0}\right) = -\frac{Q}{RT} \qquad [6]$$

Tapsell has studied the creep rates of Armco iron[16] and cast steel[17] by series of tests in which a number of temperature points were investigated at each of several stresses. The results of these tests are reproduced in Figs. 2 and 3, by plotting log secondary creep rate versus the reciprocal of absolute temperature. The lines thus determined for constant stress are essentially straight, and their slopes appear to have the same significance as those determined by the plot of ϕ_T in Fig. 1a. Each set of curves, representing various values of stress, are seen to be practically parallel, thus establishing an energy value for pure viscous creep that is approximately invariant with the stress. The value indicated for Armco iron is 97,000 cal. per gram atom and 94,500 cal. per gram atom

for the cast steel, comparing favorably with the 90,000 cal. per gram atom deduced for wrought 0.17 per cent carbon steel (Fig. 1a).   It is inter-
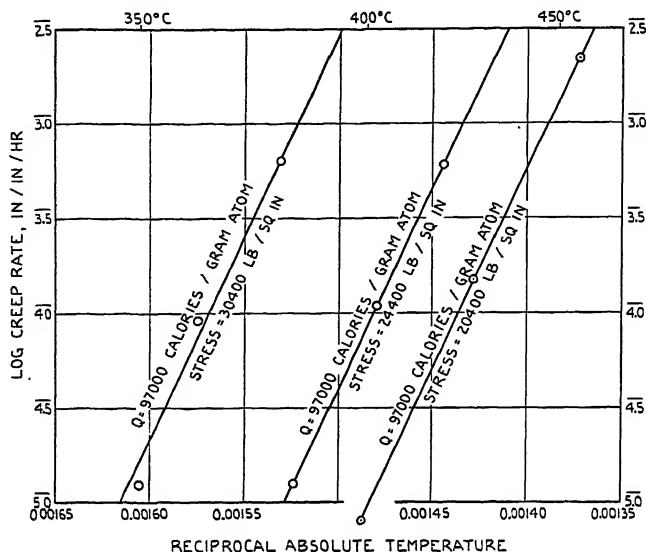
FIG. 2.—SECONDARY CREEP RATE OF ARMCO IRON AS A FUNCTION OF ABSOLUTE TEMPERATURE.
Tapsell and Clenshaw data.[16]
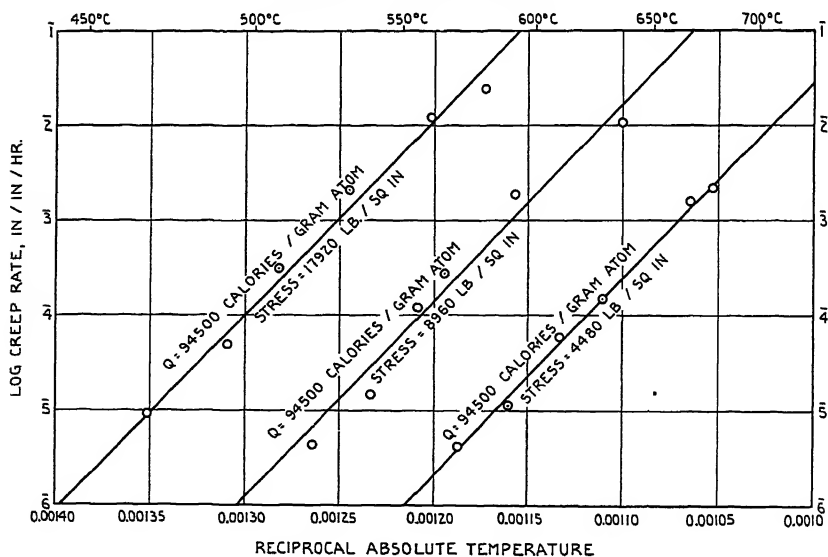
FIG. 3.—SECONDARY CREEP RATE OF CAST STEEL AS A FUNCTION OF ABSOLUTE TEMPERATURE.
Tapsell and Johnson data.[17]

esting to note that the free energy change of vaporization for iron of about 85,000 cal. per gram atom calculated by Kelley[4] from vapor-pressure data

is a value of magnitude similar to the energies obtained from the creep data. Now, whatever influence ordinary stresses may have upon the energy of viscous creep, it certainly can produce only a fractional change in the total amount involved, if the total amount is on the order of the free energy of vaporized iron. Unfortunately, the creep data are not of great enough accuracy to determine the slopes of the semilog plots with enough precision to draw precise conclusions on the effect of stress. It is obvious, though, that since the total energy value is large as compared to whatever change the stress produces, the semilog plot of ϕ_T values (Fig. 1b) will give approximately the same value as obtained from the creep-rate plot.

Effect of Stress on Secondary Creep Energy

If it be true that the curve for secondary creep rate as a function of reciprocal absolute temperature retains constant slope under variable stress, it follows that $f(\sigma)$ of equations 4 and 5 is independent of temperature and, in view of equation 6, it may be written that

$$\ln\left(\frac{v}{\phi_0\sigma}\right) = f(\sigma) - \frac{Q}{RT} \qquad [7]$$

The strain energy W as calculated from the equation for simple tension

$$W = \frac{\sigma^2}{2E} \qquad [8]$$

where E is Young's modulus of elasticity, accounts for only a minute part of the activation manifested by the increase of flowability incident to the application of stress. Calculating the strain energy for iron or steel according to equation 8, and converting to the heat equivalent, it is found that at the highest stresses for which creep rates are ordinarily observed only about 0.3 cal. per gram atom is involved. Comparing this with the 90,000 or more calories per gram atom that seems to be required for the transport of iron atoms in pure viscous creep, it is difficult to get a clear conception of strain energy as contributing appreciably to the energy of secondary creep. While it is true that strain energy increases somewhat with temperature, the temperature coefficient that this relatively minute energy can induce upon $f(\sigma)$ is indeed small unless one adopts the unlikely hypothesis of a high localized accumulating or "storing up" of strain leading to periodic slip adjustments of an eruptive nature. Even if such an interpretation of secondary creep were acceptable, $f(\sigma)$ could still be considered to possess only a relatively small temperature coefficient.

Regardless of what mechanical view of secondary creep deformation is taken to reconcile the absence of an appreciable temperature coefficient

upon $f(\sigma)$, an interesting kinetic aspect of the effect of stress upon metal is presented.   Boltzmann showed the possibility of relating thermodynamic quantities directly to mechanical quantities through statistical mechanical reasoning (see Tolman[5], p. 304) and thereupon introduced the idea that a change in entropy may accompany the change of state in the system with which it is associated.   From the classical thermodynamic point of view, the entropy of an isolated system can increase only if the maximum value has not been reached.   According to the Boltzmann conception, however, the probability of state in an isolated system determines its entropy in accordance with the equation

$$\Delta S = k \ln \frac{W_2}{W_1} \tag{9}$$

where ΔS is change in entropy, k a constant, and W_1 and W_2 probabilities associated with two states of the same isolated system.   Suppose this principle were applied by analogy to the system that is encountered in metal at constant temperature of which the state is altered by the application of stress.   This system may be considered to contain an isolated quantity of energy.   When stress is applied, a change of state occurs whereby the mechanism of activation is altered.   Thereupon the hypothesis may be made that $f(\sigma)$ is proportional to an alteration in secondary creep energy, Δ^*S.   The stress function $f(\sigma)$ is, then, defined as a ratio between Δ^*S and the gas constant R,

$$f(\sigma) = \frac{\Delta^*S}{R} \tag{10}$$

expressing thereby an empirical equivalence between stress and secondary creep energy.   Equation 7 may thus be stated in the form

$$\ln \left(\frac{v}{\phi_0 \sigma}\right) = - \frac{Q - T\Delta^*S}{RT} \tag{11}$$

The derivation of a fundamental stress function for Δ^*S is perhaps a problem involving an analysis of the deformation mechanism quite beyond the scope of this present paper.   An empirical approximation indicated by the examination of flowability diagrams for various metals, takes the form

$$\Delta^*S = c\sqrt[n]{\sigma}, \tag{12}$$

where c and n are constants.   Values for n vary trom 2 to 4.   Equation 12 suggests that the alteration of secondary creep energy that is possible through application of stress approaches a limit asymptotically, or the equivalent statement that the decrease in viscosity of the metal that stress alone produces meets rapidly increasing resistance.   Such a con-

dition is expressed by the relation

$$\Delta^*S = \ln\left(1 + b_1\sigma^m\right) \qquad [13]$$

For large values of stress, this expression is approximately the same as $\Delta^*S = m \ln b_2\sigma$, which reduces equation 11 to the form

$$v = \left(v_0 e^{-\frac{Q}{RT}}\right)_\sigma^{\left(\frac{m}{R}+1\right)} \qquad [14]$$

similar to the well-known Bailey[6] expression for secondary creep rate
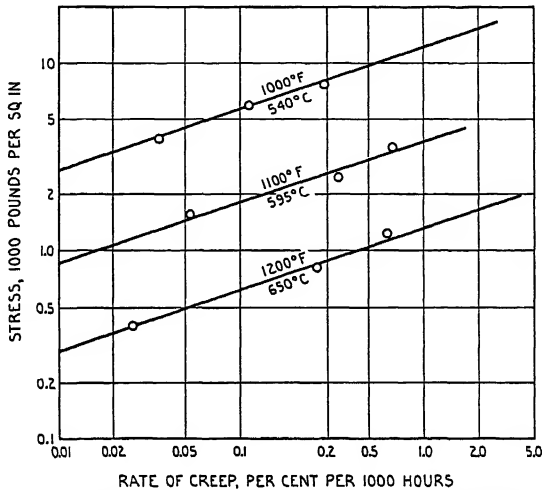
FIG. 4.—SECONDARY CREEP RATE OF 0.15 PER CENT CARBON ELECTRIC WROUGHT STEEL
PLOTTED LOGARITHMICALLY.
Clark and White data.[7]

versus stress, v_0 and v_T being constants,

$$v = v_T\sigma^n \qquad [15]$$

where

$$v_T = v_0 e^{-\frac{Q}{RT}} \qquad [16]$$

and

$$n = \frac{m}{R} + 1 \qquad [17]$$

It has frequently been observed by creep investigators that the log-log plots of creep rate versus stress are homologous in slope over a range of temperature, as shown, for example, by the Clark and White[7] tests for carbon steels (Fig. 4) at 1000°, 1100°, 1200° F., where $n = 3$, $m = 4$, and $Q = 90,500$ cal. per gram atom. It thus appears that the character of the log-log plot of secondary creep rate versus stress, over the stress

ranges where the linear relationship holds, may be given an energy interpretation similar to the one for the semilog flowability plot. Equation 11 may be considered equivalent to the Bailey equation at large stresses, but has no significance at small stresses. The theory suggests then that empirical equations in the form,

$$v = v_0(\sigma + b\sigma^n)e^{-\frac{Q}{RT}} \tag{18}$$

or else,

$$v = \phi_0 \sigma e^{-\frac{Q - Tc\sqrt[n]{\sigma}}{RT}} \tag{19}$$

afford a more general basis for dealing with secondary creep at small stresses than warranted by the Bailey equation.

MECHANISM OF CREEP

The values of Q are seen to approach the magnitude of latent heats of evaporation and heats of diffusion. As already pointed out, such large energies are difficult to reconcile with the conventional ideas of secondary creep mechanism in which deformation by slip along the planes of maximum shear provides the mode of deformation. A translatory change as provided for in a slip mechanism would be expected to correspond to energies of the order of latent heats of fusion like those computed by Dushman[3] from tensile strength data wherein plastic deformation by slip has been more clearly demonstrated than it has been for secondary creep deformations.

One is led to question whether some other mechanism than simple slip may not contribute in producing the creep strains. The simple sliding card analogy of slip planes seems an inadequate picture where secondary creep is involved. Whereas such an analogy is quite satisfactory when applied to the deformation of a single crystal, for instance, of zinc, where the basal planes furnish preferred paths for slip, difficulty is encountered when accounting for wavy slip bands of alpha-iron crystals, and other aspects of deformation in crystal aggregates. Attempts to reconcile these seemingly disorganized movements with the slip idea led Taylor and Elam[8] to liken the mode of deformation in iron crystals to a bundle of matches being moved laterally. Their picture abandons slip planes and concludes that only the direction of slip is crystallographically determined. Rosenhain[9] earlier hypothesized allotropic transformations in the solid state, in order to account for the curved slip bands. More recently, Barrett, Ansel and Mehl[21] have discussed the numerous slip systems of iron in accounting for its complex mode of deformation.

In order to explain how it is that single crystals creep at all, the suggestion is made by the Taylor[20] theory that in the ordinary metal crystals

places exist where the atoms are out of step with their immediate lattice neighbors, such regions being called "dislocations." It is held that a
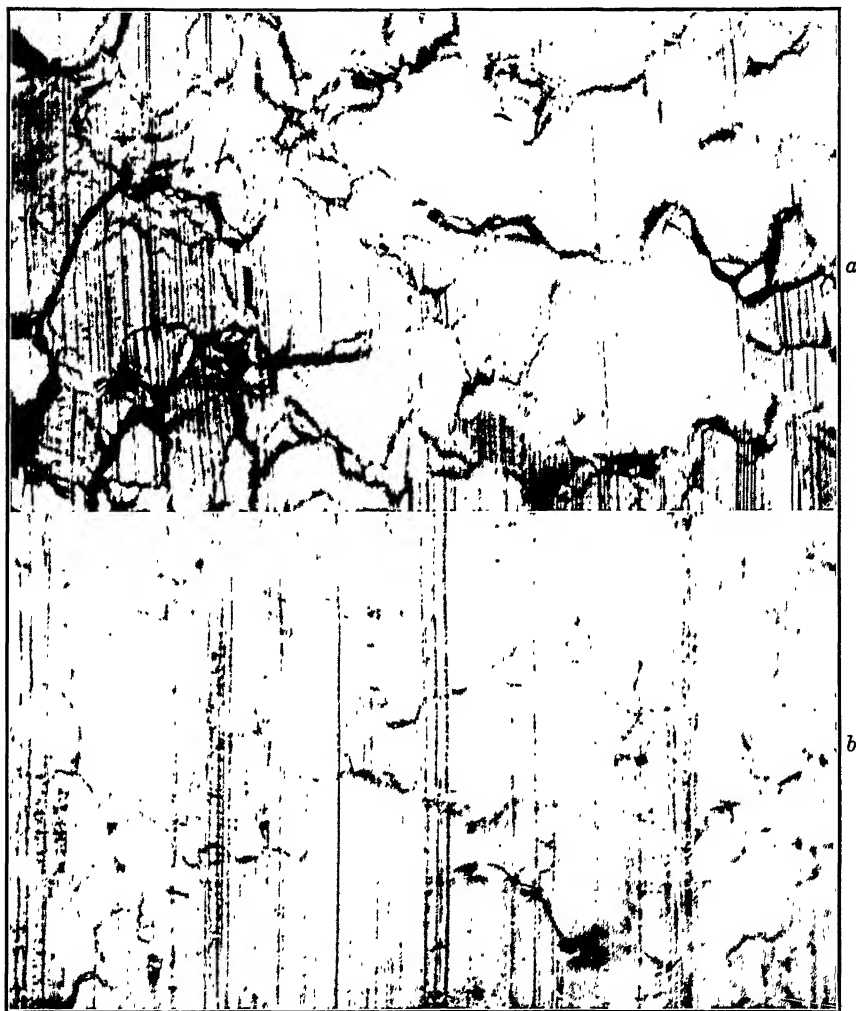
FIG. 5.—MICROTOMED SURFACE 2 PER CENT TIN-LEAD ALLOY. × 400.
 a. After 1100 hr. under steady tensile stress of 1000 lb. per sq. in., $3\frac{2}{3}$ per cent elongation. Note rotation of grains shown by change in direction of scratches left by microtome knife as it cut specimen; what seem like cracks at grain boundaries are shadows of raised edges of grain. (Moore, Betty and Dollins report.)[10]
 b. After pulling in tension machine at rate of 0.026 in. per min. to $3\frac{2}{3}$ per cent elongation. Note development of slip lines, not apparent in Fig. 5a, showing same material having equivalent elongation by creep. (Courtesy of B. B. Betty.)

small shear stress will cause such a dislocation to run along, leaving atoms in the region through which it passes advanced by one. The weakness and the flow of single crystals is explained along these lines. In poly-

crystalline metal, it would appear that the propagation of a dislocation is likely to stop at any crystal boundary. Thus, while Taylor's dislocation process affords an attractive picture for the *rapid primary flow*, an additional hypothesis seems necessary to provide for the continuance of deformation at the *uniform flow or creep rates* associated with stressed metals above their recrystallization temperatures.

Perhaps one of the most suggestive clues to the general mechanism of flow or creep deformation in polycrystalline metal is afforded by the microscopic examination made by Moore, Betty and Dollins[10] upon the surface of a specimen of 2 per cent tin-lead alloy after stressing 1100 hr. at 1000 lb. per sq. in. (Fig. 5a). No etching was necessary to bring out the grain structure of this specimen stressed in the direction of the microtome scratches, because the previously introduced scratches were found to have become segmented at the grain boundaries, traversing each grain in a slightly altered direction. The ridges bounding each grain and the varied direction of the scratches, together, indicated spatial rotations of the grains relative to each other. It is difficult to reconcile these observations with a slip process. Had slip occurred, one would expect to find the development of slip lines as shown in Fig. 5b where the deformation has been produced by plastically deforming in a tensile machine unless one accepts the somewhat dubious hypothesis that recrystallization proceeded abreast of the formation of slip bands because of the slowness of the process. The raised grain boundaries and the reorientation of each grain as a whole, together with the sharp preservation of the microtome scratches suggest that something akin to viscous flow has occurred in a layer of material enveloping each grain, leaving the crystal within unaffected. One might say that this microsection presents the appearance of the grains swimming in their own boundaries. In discussing the creep of lead alloy, Hanffstengel and Hanneman[22] contend that creep is the result of three processes: (1) strain by place exchange at the grain boundaries, (2) strain by place exchange inside the crystals by recrystallization, (3) strain by translation. Photomicrographs for iron and steel surfaces at high temperatures will greatly enhance our knowledge of the creep mechanism as a suitable technique is developed for protecting the polished surfaces of creep test specimens from oxidation while under test.

CREEP AND SOLID DIFFUSION

The *amorphous film* or layer that seems to surround the grains is to be reconciled with the modern ideas of completely crystalline material, if we adopt the hypothesis that displacements of grain-boundary atoms proceed through the kind of interchange processes that have been proposed by Jeffries[11] and others to rationalize lattice diffusions in metals and alloys. It is to be noted that the "energy of secondary creep" values, Q, shown

for the creep of metals are values of similar magnitude to heat of solid diffusion values. Brass (60 Cu, 40 Zn) tested by Tapsell, Johnson, and Clenshaw[18] has a secondary creep energy of 42,000 cal. per gram atom as shown by Fig. 6b, while the accepted value for the heat of diffusion of zinc in copper is 41,700 cal. per gram mole. If a process of atom interchange goes on in creep of copper-zinc alloy similar to the interchange of copper and zinc atoms that takes place in solid diffusion, one would expect the energies involved by the two processes to show a rough similarity.
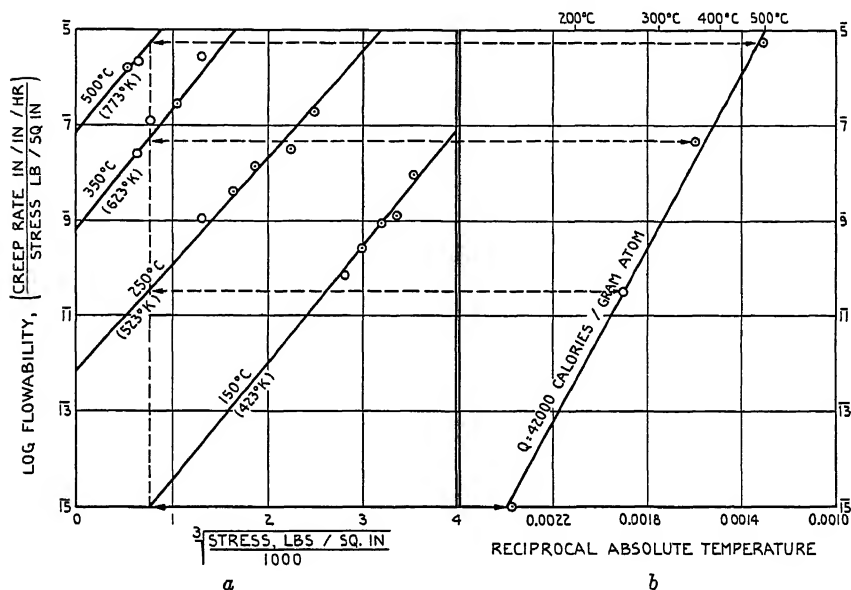
Fig. 6.—"FLOWABILITY" OF 60-40 BRASS.
a. As a function of stress.   b. As a function of absolute temperature.
Tapsell, Johnson and Clenshaw data.[18]

The idea that secondary creep and solid diffusion are related processes seems such an attractive hypothesis that a further analysis of secondary-creep data in terms of diffusion theory may be in order. The driving force of solid metallic diffusion as suggested by Mehl[12] seems to be controlled and influenced by the chemical dissimilarity between the kinds of atoms involved, but is not clearly defined. The driving force in secondary creep, however, may be defined definitely as applied stress. The specific driving force for tensile creep, as clearly demonstrated by Bailey's[13] compound-stress experiments, appears to resolve itself into shear stress. In the concept of secondary creep as a mode of viscous flow, the coefficient of flowability ϕ (equation 3) is recognized as a ratio between the secondary-creep rate and this driving force. The equation for solid diffusion is usually represented in the form,

$$\ln D = \ln A - \frac{Q}{RT} \qquad [20]$$

where D is the solid-diffusion coefficient, A is a constant, and $\frac{Q}{RT}$ has similar significance to that given in foregoing equations. Thus the characteristics of solid diffusion are defined by two empirical constants. Secondary-creep rates as discussed by equation 11 require for their definition at least four empirical constants. The energy Q, as has already been observed, seems to represent a constant that both secondary-creep and solid-diffusion phenomena have in common.

Theory of Solid Diffusion in Metals

Reasoning that solid diffusion is a process subject to activation energy, Dushman and Langmuir[14] suggested that the quantity $e^{-\frac{Q}{RT}}$ represents the Maxwell-Boltzmann probability that during an oscillation an atom will have the requisite energy to become mobile and diffuse. The value is thus identified as the minimum energy that must be exceeded before an atom can surmount its potential barrier. Assuming that each atomic "jump" from one lattice position to another involves a quantized interchange of energy, they further reason that the frequency ν of atomic oscillation is approximated by the relation

$$\nu = \frac{jQ}{N_0 h} \qquad [21]$$

where N_0 is Avogadro's number (number of atoms per gram atom $= 6.061 \times 10^{23}$), h is Planck's constant of action, 6.554×10^{-27} erg sec., and j the mechanical equivalent of heat, 4.185×10^7 erg per calorie. Upon such theoretical justification was proposed the Dushman-Langmuir expression for solid diffusion,

$$D = \left(\frac{jQ}{N_0 h}\right) \times \delta^2 \times e^{-\frac{Q}{RT}} \qquad [22]$$

where δ is the interatomic distance. Despite liberties of overgeneralization, this expression represents data on diffusion of solid metals with surprising reliability and has great usefulness for diffusion calculations where D is known at one temperature only.

Self-Diffusion Theory of Secondary Creep

Pursuing a similar course of reasoning for metal creep, as used by Dushman and Langmuir for solid metal diffusion, one is led to make the hypothesis that the quantity

$$e^{-\left(\frac{Q - T\Delta^* S}{RT}\right)}$$

also signifies some sort of a Maxwell-Boltzmann probability that the metal atoms will have the energy necessary to surmount a potential barrier. Difficulty is encountered here, however, in assigning the specific mechanism of deformation with which the probability is associated. If the view be taken that secondary creep is the result of organized shearing of atoms along crystallographic slip planes, as would be true in deformation by the Taylor[20] conception, the probability of the incidence of enough energy in a slip plane becomes a consideration. That such an organization of the energy involved in secondary creep could attain, seems, indeed, a remote possibility. On the contrary, the evidences already cited, tending to show that secondary creep deformation is not such a highly organized process, seem to favor a hypothesis that the probability involves more the state of the individual metal atom than a set of lattice points. The particular location of the atom, with reference to lattice imperfections such as grain boundaries, mosaics, and stranger atoms or molecules, exerts perhaps the determining influence whether migration or self-diffusion is within the realm of probability. Upon this view, only certain disadvantageously situated atoms are apt to be involved at any one time in effecting the observed rate of creep strain while the multiplicity of lattice imperfections determines the eligible number of atoms contributing to secondary-creep strain. If only the direction of slip is crystallographically determined, secondary tensile creep by such a process would proceed through atom migration in the shear stress directions and most readily in the directions of maximum shear stress.

Such a mechanism, we must recognize, however, would only be expected to yield a uniform rate of creep, under the condition of recrystallization, since only above the recrystallization temperature would the concentration of lattice imperfections be expected to remain approximately constant as creep proceeds. Equation 11, therefore, would not be expected to correlate creep rate below the recrystallization range. Under strain-hardening conditions, the changing density of lattice imperfections varies with the flowability value ϕ_0 as well as the stress function, $f(\sigma)$. Thus the problem of correlating secondary-creep rates under strain-hardening conditions involves the additional considerations of a changing *eligibility* and the consequent changing probability. Since these relations undoubtedly change rapidly with temperature, the $e^{-\frac{Q}{RT}}$ term cannot be assigned the significance it has under recrystallization conditions. A notable exception to the metals for which tensile creep data can be correlated by equation 11 is austenitic chromium-nickel steel. The explanation perhaps lies in the fact that this alloy strain-hardens even at high temperatures. Characteristically different from ferritic iron, this material shows no wavy slip bands when plastically deformed.

It may well be that the exceptional high resistance of this material to secondary creep is attributable to the fact that its deformation is governed to a greater extent by organized movement of lattice points than by deformation of the solid diffusion type.

The temperature coefficient of tensile creep rates in the strain-hardening range thus seems to present a problem of greater complexity than under conditions of recrystallization.   Of interest in this connection is the theory of rate of plastic deformation proposed by Becker[15] and extended by Orowan[25] in which the gliding of slip planes under the influence of thermal motion is treated as an effect governed by the law of probability. Gliding at a definite velocity, in Becker's conception, occurs at a shearing stress s, which is less than the limiting stress S.   A relation for rate of plastic deformation proposed is in the form

$$\ln \left(\frac{v}{v_0}\right) = -\frac{a(S - s)^2}{RT} \qquad [23]$$

where a is a constant involving the modulus of elasticity and the quantity $a(S - s)^2$ represents an amount of energy similar to Q.   This expression is derived on the idea that the strain energy, previously discussed, is a measure of the energy required for plastic deformation.   The gliding is assumed to be similar to that of two toothed surfaces.   When this theory was originally proposed in 1926, few creep data were available. The objections to equation 23, in view of consideration given to the magnitude of strain energy and the more recent creep data leading to equation 11 or equation 19, are obvious.

Becker recognizes, however, that in recrystallization the disturbed lattice approaches the ideal state by a mechanism of atomic interchange, for which reason he postulates that the probability of interchange is proportional to the term $e^{-\frac{Q}{RT}}$, where Q represents the difference in potential energy of the atoms in the deformed lattice as compared with the undeformed.   The values of Q for recrystallization after cold-working and grain-growth processes, which have been shown upon this basis by van Liempt[23] and by Dushman,[3] are of the same order of magnitude as those computed from rate-of-creep or plastic-deformation data.   The points of view expressed by Becker, van Liempt or Dushman are thus in harmony with the idea that the migration of atoms in the process of plastic deformation is related to kinetic probability.

An Equation for Secondary Creep by Self-diffusion

If creep strain bears relationship to the probability of atom migration in a crystallographically determined direction, a companion expression for the Dushman-Langmuir equation applying to tensile creep rates may

also prove useful. Restricting consideration to the uniform secondary tensile creep rates above the recrystallization temperature, such an expression may be discussed. Considering creep-strain rate dimensionally, it is defined as a time rate of *fractional change*, the fraction comprising unit change of length, a ratio between two lengths. Thus the only physical dimension of creep-strain rate is reciprocal time. The frequency of oscillation as determined from the ratio between energy Q and the action constant h likewise has reciprocal time for its dimension. The major component of the fractional change to be associated with an atomic jump in a crystallographic direction may be identified with the interatomic "jump" distance δ, which approximately measures a dislocation in the direction of strain proportional to $\delta \sin \theta$, where θ is the angle between the crystallographic direction and the direction of strain. By Bailey's hypothesis of strain by maximum shear alone, this displacement should approximate $(\frac{1}{2}\sqrt{2})\delta$, which constitutes the fractional change when multiplied by the number of potential points of dislocation per unit length. In this connection, these points of dislocation are understood to be more likely to be crystal and phase boundaries than the "out of step" regions of the Taylor[20] theory. This idealization embodied in a number designated as λ may be considered a constant for the material when under conditions of recrystallization, but is subject to variation with strain under strain-hardening conditions or with time in structurally unstable materials. In unalloyed metals and solid solutions, λ should have a magnitude approximating the number of lattice imperfections, *mosaics*, or grain boundaries traversed per unit length. Since λ has reciprocal length for its dimension, the term $(\frac{1}{2}\sqrt{2})\delta\lambda$ comprises a dimensionless group equivalent to the strain group $\frac{\Delta l}{l}$, where l is the length under strain.

Referring to the quantum expression 21, we may write a term $\left(\dfrac{jQ}{N_0 h}\right)\left(\dfrac{1}{2}\sqrt{2}\right)\delta\lambda$ to be interpreted as secondary-creep rate under the hypothetical circumstances at which the atoms at potential points of dislocation have become activated to an extent overcoming their cohesional forces. Such might be the state of the system where ϕ of equation 3 approaches values associated with either fusion temperature, or stress equivalent to the molecular cohesive force. The flowability constant ϕ_0, it would seem, may be analyzed into a ratio between the quantum term for fractional time rate of change and a stress constant σ_0 having the magnitude of molecular cohesive force.

The probability of dislocation for material in tensile creep, as expressed by equation 11, depends not only upon a function of temperature, as in the theory of diffusion, but in addition is dependent on an alteration of secondary-creep energy effected by stressing. This alteration, according

mental side of creep investigation to warrant the prediction of creep behavior upon any mathematical formulation of the problem.

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DISCUSSION

(John S. Marsh presiding)

J. E. DORN,* Columbus, Ohio (written discussion).—It is surprising that a problem as complicated and difficult as creep is at all amenable to mathematical analysis. Mr. Kanter's pioneer work in this field is worthy of the serious attention of engineers and metallurgists interested in creep, diffusion, and related subjects. As a more complete and accurate knowledge of creep is obtained, some of the concepts presented in this paper may require modification. Nevertheless, I believe that this paper will constitute an important stepping stone to subsequent theoretical considerations of creep rate.

There are, however, several expressions in the text that seem questionable. Equation 6 states that for $T = \alpha$ the flowability equals the flowability for $T = 0$. In contrast, however, Fig. 2 shows that the flowability increases with temperature. This inconsistency may be rectified by replacing φ_0 by φ_α, the flowability at infinitely high temperatures. A semitheoretical derivation of expression 6, assuming that φ is the equilibrium constant for this physical phenomenon and applying the Gibbs-Helmholtz relationship, will show that φ_0 should be replaced by φ_α. This derivation is valid only when Q is independent of the temperature.

Various theories for diffusion result in equations that have the form

$$D = Ae^{-\frac{Q}{RT}}$$

A, in general, may be expressed as $\nu\delta^2$ where ν is the mechanical frequency of the diffusion process and δ is the jump distance. According to Dushman and Langmuir

$$\nu = \frac{Q}{Nh}$$

This ν, however, is not the frequency of the mechanical process but the frequency of the wave associated with this process. It is not surprising, therefore, that A when calculated on the basis of this theory is 20 to 200 times greater than the experimentally determined value. The van Liempt equation in which

$$A = \frac{8}{3\pi}\nu\delta^2 \qquad .$$

is more accurate. Here ν represents the mechanical frequency of the atom on the basis of Einstein's theory of the solid state. This equation yields values of A which are 2 to 6 times greater than the experimentally determined values. We are led, therefore, to the conclusion that the relationship between the frequency of the diffusion mechanism and the characteristic frequency of metals is more complicated than van Liempt assumed. Recently Dorn and Harder presented a theory of diffusion in which

$$\nu = \frac{1}{\tau}$$

where τ is the time required for a jump. Since τ is determined by experiments on diffusion, agreement between theory and experiment is one to one. It may be possible to express τ in terms of more fundamental quantities but at present too little is known about the jump mechanism to do so.

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* Research Associate, Battelle Memorial Institute.

Mr. Kanter has made the assumption that the frequency of the wave associated with the phenomenon of secondary creep is equal to the true mechanical frequency of this process. Quantum mechanics shows that this equality is rarely true. We must assume, therefore, that the coefficients of the exponential in equations 25 and 26 of the text are highly questionable. This does not alter the validity of

$$\varphi_T = A e^{-\frac{Q}{RT}}$$

where A is some constant to be determined from experiments on secondary creep. An important theoretical advance in the study of creep may result from the experimental verification of the question concerning the equality of the heat of flowability and the heat of self-diffusion.

I am certain that engineers and metallurgists, alike, will be looking forward to future papers by Mr. Kanter on this subject, especially an evaluation of A in the above equation on the basis of a mechanical picture of the process of secondary creep in terms of the fundamental quantities involved.

B. B. BETTY,* Huntington, W. Va. (written discussion).—Mr. Kanter's thermodynamic approach to this problem is a valuable supplement to the mechanistic study of creep phenomena. It should not, however, be regarded as a substitute for it. A study of the crystallographic mechanism of creep strain is a necessary pursuit if we are to rely, even in part, on the science of metallography in eventually establishing a practical control of creep properties of metals. I have spent several years in creep testing and am cognizant of the fact that if ever such a practical control method is worked out, it is certainly not expected to be a simple one.

While the size and shape of grains have been found to have some bearing on the creep resistance of metals, their determination alone has not afforded an adequate and sufficient basis for the prediction of creep rates. We still must resort to a laborious test procedure for reliable values. The very expense and time required for these tests emphasize the value of Mr. Kanter's paper.

If such a thermodynamic analysis reduces, even in a small way, the amount of testing required to obtain a given amount of information about the creep resistance of a metal, or if, for a given amount of testing, it enables us to gain more knowledge of that creep resistance, the author has made an important contribution to the literature. It is hoped that he will continue his studies in this field. Crystallographic mechanism of creep has lent itself to the study of the effect of stress upon creep rates, but because of laboratory difficulties has offered little information on the effect of temperature on such rates.

The idea of grains swimming in their own boundaries cannot be regarded as a complete picture of the mechanism, as the author is well aware. It is inconceivable that such irregularly shaped polyhedra as these grains are known to be can undergo such large spatial rotation without suffering considerable deformation within themselves. Some as yet unpublished work on the creep of annealed single crystals of lead, at the University of Illinois, indicates strongly that the fundamental shape of the creep-time curve for polycrystalline metal has its origin in the properties of the grains themselves.

Furthermore, there is some evidence, from experiments performed in England, that the surface condition has much to do with the rate of deformation of single crystals. From this it would seem that both the crystal boundaries and the internal state of the crystals play important roles in the creep resistance of commercial metals. Certainly, after having examined Fig. 6 one can have little doubt about the important

* Metallurgical Department, International Nickel Co.

role played by the boundaries. Owing to the more or less random orientation of grains and to the experimentally observed fact that slip in a grain occurs in a definite crystallographic direction, it must be concluded that the grain boundaries offer considerable restraint to slip within the grains, at least below the recrystallization temperature. The angular difference in the directions of slip of two adjacent crystals offers the most plausible explanation for the forces necessary to produce such grain rotations as may be observed in Fig. 6.

Failure to observe slip lines in lead deformed under creep conditions does not seem to afford sufficient proof that slip does not occur. I have interpreted this to mean that the slip was so well distributed throughout the crystal that an insufficient amount took place on any one group or band of planes to produce visible markings at the surface.

Such a distribution of slip is probably promoted by the movement at the boundaries. The straightness of the microtome scratches still does not exclude the possibility of slip having taken place, for if slip were more or less uniformly distributed, and if it occurred on a set of parallel planes, straight lines on the surface would remain straight.

It seems to me that, whatever physical explanation we make of the creep phenomena, we must consider the effect of the exchange at the grain boundaries plus the effect of distortion within the crystals. This explanation pertains to the effect of stresses on the creep mechanism. Let us now see how an increase of temperature might affect the picture. In the first place, since the grain boundaries contain the material having the lowest melting point in a metal, it does not seem unreasonable to expect that they would display a more pronounced response to an increase in temperature. Secondly, the microstresses at the boundaries arising from the angular differences in directions of slip in two adjacent grains would give to the material in the vicinity of the boundary a higher energy level. When one further considers the difficulty of applying a mechanistic theory to the deformation of the more or less disorganized boundary materials, a thermodynamic attack upon the problem would seem not only appropriate but to offer definite promise of fruitful results.

E. R. PARKER,[*] Schenectady, N. Y. (written discussion).—Mr. Kanter has gained our admiration with this unique interpretation of high-temperature creep data. This contribution has given us an excellent start along the road to a better understanding of high-temperature plastic flow.

There are a few corollaries of this interesting phenomenon. The data in Fig. 7 were taken from a paper by White, Clark and Wilson,[26] also presented at this convention. Here, on a log-log plot, the hours to failure have been plotted against stress for two steels. Only the data not influenced by oxidation of the steel have been used, and these data have been extrapolated for the long-time values. In Fig. 8 the hours to failure have been plotted against the reciprocal of the absolute temperature, at various stresses, to give a straight-line relationship. The time for failure is an approximate measure of the creep resistance of a steel, which is an inverse function of flowability. This follows from the value obtained for the energy involved, 95,000 cal. per gram atom, which is the same as that shown by Mr. Kanter for the tensile creep rate of steel. It is interesting to note that the energy is not materially affected by moderate alloy additions.

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[*] Research Metallurgist, General Electric Co.

[26] E. A. White and C. L. Clark: The Rupture Strength of Steels at Elevated Temperatures. *Trans.* Amer. Soc. Met. (1937) 868; and *Trans.* Amer. Soc. Met. (1938) **26**, 60.
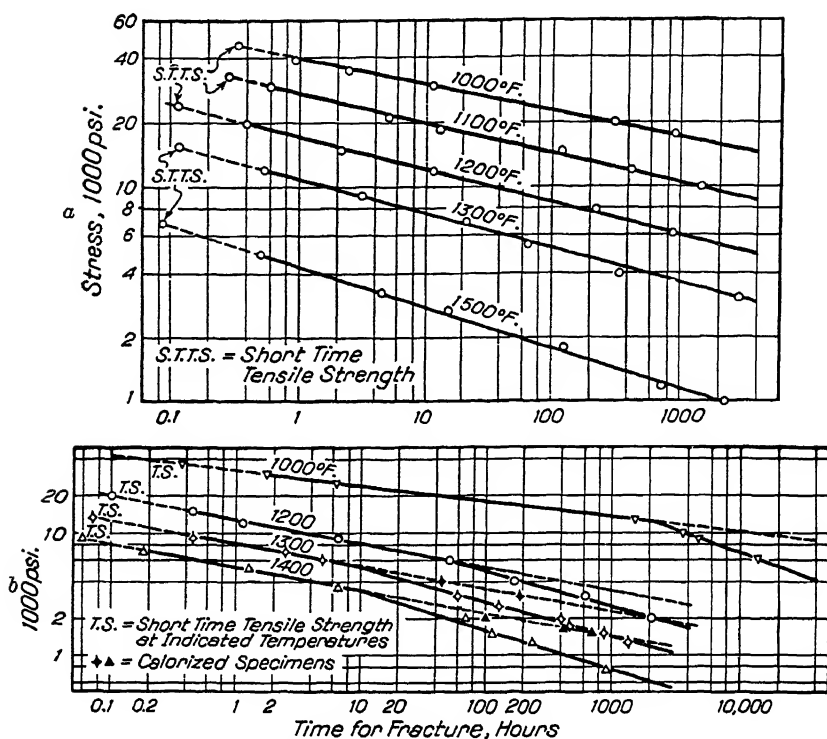
FIG. 7.—STRESS-RUPTURE CURVES FOR (a) CR-MO-SI STEEL AND (b) STEEL SAE 1015 (EL).
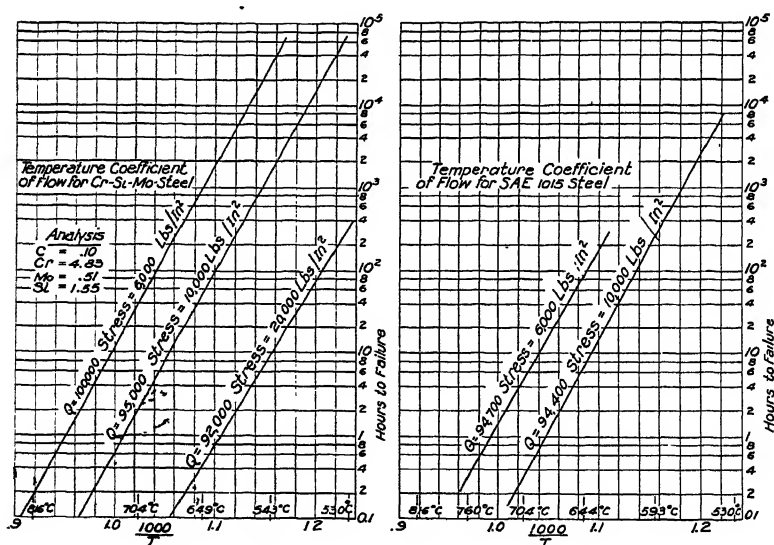
FIG. 8.—TEMPERATURE COEFFICIENT OF FLOW.

This energy of flow should not be confused with the energy of rupture, which is much lower. In Fig. 9, the log of the tensile strength for various strain rates has been plotted against the reciprocal of the absolute temperature. Here, again, a straight line results, but the slope of this line is much smaller, yielding an energy value in the neighborhood of 15,000 cal. per gram atom.

H. F. MOORE,* Urbana, Ill.—An engineer who has a very high respect for metallurgists and physicists would like to present a very crude cartoon, which occurred to him in his three times reading of Mr. Kanter's paper. The picture gathers around the idea of "eligible atoms," or, as I prefer to say, "eligible regions" for creep. It seems preferable to think of creep not as a phenomenon of an isotropic homogeneous material but as a series of localized happenings.

Creep at low stresses seems to resemble a viscous flow of the metal. We then add stress at a constant temperature. As the last discussion showed, the stress would
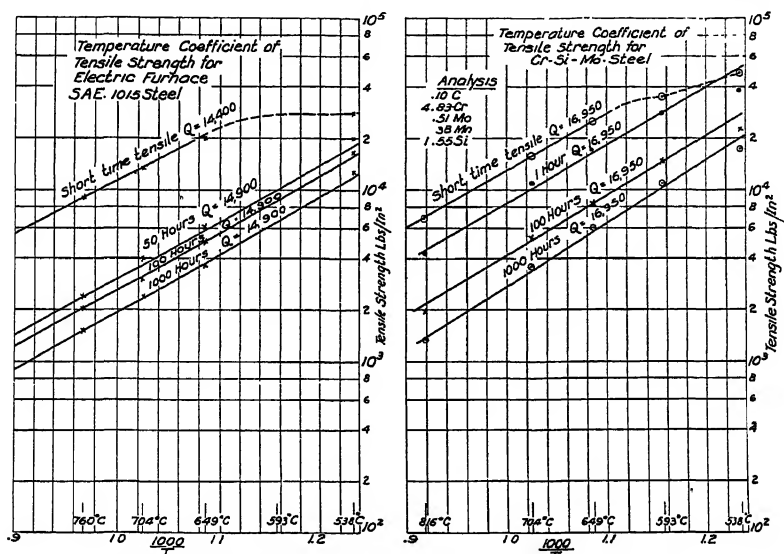
FIG. 9.—TEMPERATURE COEFFICIENT OF TENSILE STRENGTH.

decrease the energy necessary for creep-diffusion of the atoms to take place, or we might, using an extremely crude illustration, say it reduced the entrance fee for the "eligibles" into "active" membership of the order of creepers. We could still have viscous flow at each one of the eligible regions, with creep rate proportional to stress *for each region,* but now creep is taking place at more locations and the *total* creep of the piece increases faster than would be indicated by proportionality of creep rate to stress. In the same way, if I understand Mr. Kanter correctly, if we add temperature we give to his "eligible" atoms greater energy—that is, greater ability to pay their entrance dues as active members of the order of creepers.

In both these ways viscous flow would be able to take place over increasing areas, so that for constant temperature the total creep might well come to follow a relation somewhat like Bailey's power equation, $v = AS^n$, in which v is the creep rate; S the stress and A and n are experimentally determined constants. However, for lead alloys the speaker has not found n to be a constant, at least for low stresses.

* Research Professor on Engineering Materials, University of Illinois.

R. G. STURM,* New Kensington, Pa. (written discussion).—This stimulating paper presents a most interesting summary of recent papers by a number of authors touching upon the physics of metals. The author shows that, according to his computations, comparisons between the results obtained from quantum physics and observations in creep indicate that certain relationships exist between the fundamental physical constants for metals and the creep rates of these metals.

The writer would by no means question the existence of relationships between the physical properties of materials and these fundamental constants but it would seem that further consideration should be given to the basis for choosing the particular properties, such as the creep rates. Experimental data certainly indicate that for a given stress the creep rate of a material is much greater during the first few seconds after application of load than it is after appreciable time has elapsed. The author indicates that he considers the question of viscous creep at small stresses and assumes that the metal is undergoing a constant rate of strain. This, in turn, requires that the creep-time curves are straight lines. Available test data do not seem to justify a general basic assumption that creep at design stresses is proportional to the elapsed time, or that the creep rate is independent of time.

Some tests[27] indicate that the creep at stresses that may be used in design progresses with a gradually decreasing rate and may be expressed as a power function of time as

$$C = C_1 t^K$$

where C = creep at any time t at any stress s.

C_1 = creep after one unit of time has elapsed for the given stress.

t = elapsed time expressed in whatever units are desirable.

K = a constant for the material at the temperature considered.

In view of the fact that there seems to be some question as to the validity of the hypothesis upon which the author has made his comparisons, the writer is inclined to heartily agree with his concluding sentence rewritten as follows: "It is to be distinctly emphasized that too little has as yet been done on the experimental side of creep investigation to warrant the prediction of creep behavior solely upon any mathematical formulation of the problem."

E. U. CONDON,† East Pittsburgh, Pa. (written discussion).—The theory of diffusion as presented in the first paper[28] and also some of the ideas in Mr. Kanter's paper are closely related to those presented by Prof. H. Eyring, of Princeton, in a recent paper.[29] Eyring developed a theory of viscous and plastic flow from the point of view of statistical mechanics, which I regard as the most important contribution to our understanding of these things that has yet been made. A clear and elementary presentation of it will be found in an article by Smallwood,[30] where application is made to plastic deformation of rubber.

The theory provides a formula for shear strain rate of the form

$$A e^{-E_0/kT} \sinh \frac{fV}{kT}$$

in which f is the shearing stress, E_0 is the activation energy for displacement of an atom from one equilibrium place to the next, k the Boltzmann constant and T the absolute temperature. A and V are constants, which are related by the theory in quite definite ways to parameters of the lattice structure.

If $fV \ll kT$ for all values of the stress, one has approximate proportionality of the strain rate to the stress as in ordinary viscous liquids. On the other hand, if $fV \gg kT$ we have $\sinh \dfrac{fV}{kT} \sim \dfrac{1}{2} e^{-fV/kT}$ and the formula gives the same type of exponential dependence of creep rate on stress that is found empirically, as has been emphasized in Mr. Kanter's paper.

I have made some preliminary calculations on the applicability of Eyring's ideas to the creep-rate problem, which have met with some success, but it would make the discussion too long to attempt to present them here. It is hoped to publish them shortly.

E. OROWAN,[*] Birmingham, England (written discussion).—Mr. Kanter blames the Becker formula for not conforming with measurements of the secondary creep rate of certain kinds of iron and steel. This lack of accord, however, is not at all surprising, since the formula relates to a phenomenon quite different from secondary creep; namely, to the plastic gliding of crystals.

On applying a load to a polycrystalline metal, glide processes will, of course, start in its crystal grains; the neighboring grains, however, having different orientation, impinge upon each other so that at their boundaries higher stresses arise, which act against further gliding. A similar effect occurs inside crystals with more than one set of glide planes; here "glide zones"[31] representing one set of glide planes act as obstacles to gliding along glide planes traversing them.[32] In order to overcome these obstacles, the load must be increased (strain-hardening). If the load is constant, the rate of deformation decreases as the resistance of the grain boundaries (and of traversing glide zones) against gliding increases (primary creep). The rate of creep would asymptotically tend toward zero if the stresses at the grain boundaries were not in course of time released by a rearrangement of the atoms taking place by preference in the areas bearing the highest stresses. This process of rearrangement is essentially the same as in strain-hardening recovery (*Kristall-Erholung*) or of recrystallization: under the influence of thermal fluctuations atoms or groups of atoms pass over into new positions representing lower energies and lower stresses than the previous configuration. In conveying the atoms into new positions energy barriers must be overcome (in absence of such a barrier the new position could have been reached without the help of a thermal fluctuation; in other words, the previous configuration corresponding to a higher energy would not have been realized at all, except perhaps for a very short time).

If A is the height of such an energy barrier, then, according to Boltzmann's formula, the probability of the rearrangement taking place in a certain time interval is proportional to

$$e^{-\frac{A}{kT}}$$

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[*] Physics Department, University of Birmingham.

[31] E. Orowan: *Ztsch. Physik* (1934) **89**, 634; *Schweizer Archiv ang. Wiss. u. Technik* (July 1935).

[32] As a consequence of this the "strain-hardening curves" of crystals with more than one set of glide planes are quite different from those of crystals possessing one set of glide planes only. See Fig. 5 of E. Schmid: *Physik. Ztsch.* (1930) **31**, 893.

After the rearrangement the energy and the stresses in the surroundings are diminished so that without increasing the load additional gliding can occur until the stresses at the grain boundary in question have again reached values sufficient to prevent further gliding. This is clearly the mechanism of the secondary creep; it follows directly that the temperature dependence of the secondary creep rate is given by a formula

$$v = Ce^{-\frac{A}{kT}}$$

if the "activation energy" A is considered as constant for all rearrangement processes. Actually A depends on the structure of the stressed place and thus v is given by a sum of such expressions.

The factor C does not depend explicitly upon the temperature; it represents the extension of the stressed boundaries as well as the average amount of creep produced by a single rearrangement process. Thus C depends upon the glide system of the crystal, upon the grain structure of the metal, upon the load, etc., in a very complicated manner.

We see now that the Becker formula could only apply (although, in general, not directly[31]) to the very first stage of the *primary* creep but not to secondary creep since the rate of the ideal secondary creep cannot depend on the rate of gliding, which would be exhibited by a freely gliding crystal, but only on the rate at which the obstacles to gliding are removed by thermal agitation.

Mr. Kanter's objection that a self-diffusion theory (or, in our words, an atomic rearrangement theory) of creep could not work below the recrystallization temperature, obviously does not apply to our picture of creep. As illustrated by the well-known Czochralski diagram, recrystallization temperature decreases with increased cold-working. Now the amount of cold-working as measured by internal stresses and lattice destructions is very much greater at the grain boundaries where the glide planes of two crystals meet or at the crossing of glide zones, than its average value for the bulk of the material. Thus we have to assume that at the grain boundaries atomic rearrangements are very frequent even at temperatures at which macroscopically observable rearrangements (recrystallization) do not occur.

The question why a possible microscopic recrystallization once started at the grain boundary does not proceed into the grain itself can easily be answered by referring to some important results of P. A. Beck and M. Polanyi[33] concerning the "consumptibility" of crystalline materials by recrystallization. These authors showed that recrystallization if started at an artificially "inoculated" point (e.g., by scratching with a pin) cannot proceed into the bulk of the material unless its cold-working exceeds a certain limit. Above this limit the material is "consumable" in the case of artificial inoculation; it cannot, however, undergo spontaneous recrystallization unless a second, higher, limit of cold-working has been reached (for a certain temperature of annealing).

We see that our present knowledge of the plasticity of crystals gives at once a very simple picture of the mechanism of creep. So we must ask why the tremendous number of papers dealing with this subject presents such a confounding complexity of views about the nature of this phenomenon, instead of its straightforward explanation.

The reasons seem to be that creep phenomena have so far been investigated only in terms of old-style technology. For a number of decades, the usual way of tackling similar problems was to apply simple and exact tests (e.g., tensile tests) to the very complex and impure materials used in industry, and then to subject the results of these

[33] P. A. Beck: Effect of Reversed Deformation on Recrystallization. *Trans.* A.I.M.E. (1937) **124**, 351.

tests to a subtle mathematical analysis. As to the prospects of this way of proceeding, we need only realize that a piece of iron is far more complicated a structure than, for example, a watch. Now imagine subjecting a watch, without opening it, to a compression test; further, trying to draw mathematical conclusions from its undoubtedly very interesting stress-strain curve, and, finally, dissolving the watch in acids to determine its chemical composition. Although the most accurate experimental tools may be used, and the highest degree of mathematical skill displayed, I doubt whether in this way much valuable information could be obtained about how the watch is working and how it could be improved. A much more promising way is to take the watch to pieces, to observe its design and then to study the technological properties of its parts. Translated into the terms of our present problems: We must first learn the properties of single crystals, in particular the laws of their plasticity; then we may proceed to a study of polycrystalline metals with more chance of succeeding than hitherto.

J. J. KANTER (written discussion).—In presenting this paper, the writer sought primarily to focus attention upon certain of the possibilities of interpretation and analysis presented by the metallic creep problem which lend themselves to the concepts of atomic physics. Judging by the stimulating discussion, constructive criticism, and recent citations in metallurgical literature, this paper has well served its prime purpose—namely, that of finding common ground upon which the metallurgist and theoretical physicist might meet. It is to be expected that any new adaptation of theoretical notions will not meet with detailed acceptance. The central idea, however, that creep rates have an aspect that should be considered from the standpoint of chemical activation and reaction rate has not been seriously questioned. The detail around which a reaction-rate theory for the creep of metals is to be built raises, of course, numerous questions regarding the mechanism of creep deformation to which we do not as yet have adequate answers. As to these all-important details, the writer would keep an open mind toward any modifications in the reaction-rate theory of creep which discussion and further experiment show to be desirable.

The writer is inclined to agree with Dr. Dorn that the frequency determinable from the energy of a diffusion process is not the correct mechanical frequency of that process. In its present state of development, however, creep data can be expected to yield only an "order of magnitude" agreement upon any dimensional equation that might be set up, and any of the current concepts with regard to the diffusion mechanism might be made to fit the data with equal plausibility within the order of experimental precision which has been attained. Dr. Dorn's point concerning the correct definition of the flowability constant is well taken, and the subscript should be replaced by one referring to indefinitely high temperature.

Study of the crystallographic mechanism of creep deformation, as Mr. Betty points out, is certainly indispensable to the understanding and practical control of creep properties. It is to be hoped that future creep studies upon steels, brasses, and other alloys, of the kind which Mr. Betty has made upon the surfaces of lead and lead alloy, will be made. The development of the surface features reveals a type of information about grain-boundary flow that is lost to examinations upon metallographic sections of creep-deformed materials. New testing techniques are needed for the preservation of surfaces of creep-test bars against oxidation and other chemical effects at elevated temperature, so that the development of surface features will not be obliterated or obscured. Lead and lead alloys, which undergo substantial creep deformation at temperatures at which oxidation is not a factor, have made possible the obtaining of the desired information without special precautions. It seems well worth the while of creep investigators to make an effort to obtain parallel information for iron and steel at elevated temperatures. Since both grain-boundary flow and

crystallographic slip are undoubtedly present in all plastic and creep deformation, studies to determine the relative degree of their effects under varying circumstances are of fundamental importance.

The confirmation of the magnitude of the creep energy for steels from "time-to-rupture" data, which Mr. Parker has shown, is most gratifying in view of the weight it lends to the idea of rationalizing the temperature coefficients of tensile creep in terms of activation energies established as fundamental constants of the materials dealt with. Derivation of Q values upon this basis, however, may not be as concisely defined as those computed directly from creep rates. With regard to the derivation of the energy of rupture from the decrease of the creep strength with temperature, the concept does not seem to be clear-cut. Although Dushman has used the change in rupture strength with temperature as an argument for deduction of the energy of rupture, it is not entirely clear wherein a reaction rate is directly represented by either rupture strength or creep strength. In a recent discussion to a paper by E. L. Robinson,[34] the writer proposed a method whereby creep energy values might be derived from the creep stress versus temperature relationship, using as a basis equation 7 of the paper under discussion. Suppose it is desired to apply equation 7 to the problem of the effect of temperature variation on the creep strength of steels. The variable is then defined as a constant v_0 and $\dfrac{v_0}{\phi_0} = \sigma_0$. Furthermore, since a range of stress considerably above zero is usually considered, a stress function compatible with equation 5 can be chosen by letting

$$f(\sigma) = (n - 1)ln\left(\frac{\sigma}{\sigma_0}\right)$$

where n is the same slope of a log-log plot as shown in Fig. 4 of the paper and σ_0 is the stress constant. Substituting these values, equation 7 becomes

$$ln\left(\frac{\sigma}{\sigma_0}\right)^n = \frac{Q}{RT}$$

or, written as an explicit function of stress:

$$\sigma = \sigma_0 e^{\frac{Q}{nRT}}$$

The power n from the log-log plot assumes an interesting significance in connection with this equation. Experimental values of n vary from unity to as high as 20, depending upon the material, the temperature, and even the portion of stress range considered. The partition of energy under varying crystallographic restraints seems to influence the magnitude of the value. In general, as temperature increases and the molecular or lattice restraints grow weaker, it is found from creep data that the values of n diminish and tend to approach unity as a limit. This decrease, however, does not always proceed uniformly, presumably due to phase changes which may occur. Considerable variation in the slopes of the log-log creep rate versus stress plots is found between various temperatures as illustrated in Fig. 10. It is interesting to note that for both ferritic and austenitic steels the n values reach maxima at temperatures corresponding to the points of most intense temper embrittlement for the respective steels. These are also the temperatures usually associated with strain-hardening relief and "equicohesion." All these facts are very suggestive of the thought that transitions are in progress at these temperatures which may well lead to anomalies in

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[34] E. L. Robinson: Effect of Temperature Variation on the Creep Strength of Steels. *Trans.* Amer. Soc. Mech. Engrs. (1938) **60**, 253–259.

the observed values of n. If n is influenced by the partition of energy of deformation, it is not surprising to find it rising to a maximum in the vicinity of a critical temperature. The equation suggests that for a diagram plotted as Mr. Parker's Fig. 9 the energy derived is to be regarded as $\frac{Q}{n}$. It follows from the data in Fig. 10 that the creep stress curve has an inflection point at the temperature corresponding to the maximum of the curve representing the index n. The energy Q then is proportional to the product of the slope and the value of n for the corresponding temperature, as illustrated in Figs. 11 and 12.

It is to be noted particularly that in austenitic chromium-nickel steel energy values (268,000 cal. per gram mol., Fig. 12) are far greater than can be attributed to the activation associated with the migration of a single atom. Such energy values
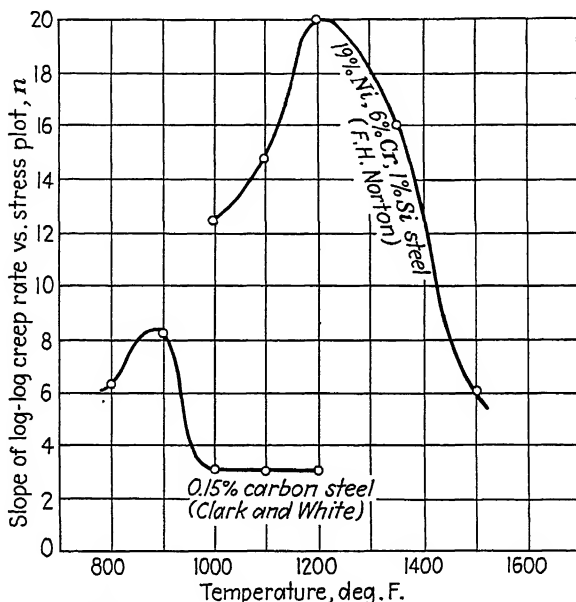
FIG. 10.—RELATION OF TEMPERATURE TO CREEP RATE AND STRESS.

suggest that creep deformation involves the activation of a molecular group or "eligible region," which in the case of nickel-chromium-iron austenite is perhaps three or four times as large as in the case of ferrite. In other words, austenite, ferrite, and different modifications of either undoubtedly vary in character.

The idea that increase of stress increases the "eligible regions" for creep has been very aptly emphasized by Professor Moore. We have only to admit that an increased rate of deformation by slip gives rise to an increased number of crystallites in metal, and the eligible regions for creep are thereby also increased through the rise in concentration of the intergranular material which we conceive as participating in viscous boundary flow. It is not surprising under this circumstance to find the different metals exhibiting widely varying functional relationship between creep rate and stress. The further possibility that stress application may also contribute to the reduction of the "entrance fee" for the eligibles is a view in justification of the form used for equation 11.

The treatment of viscosity data for fluids from the standpoint of reaction rate by Eyring is an idea having a great deal in common with the present discussion on
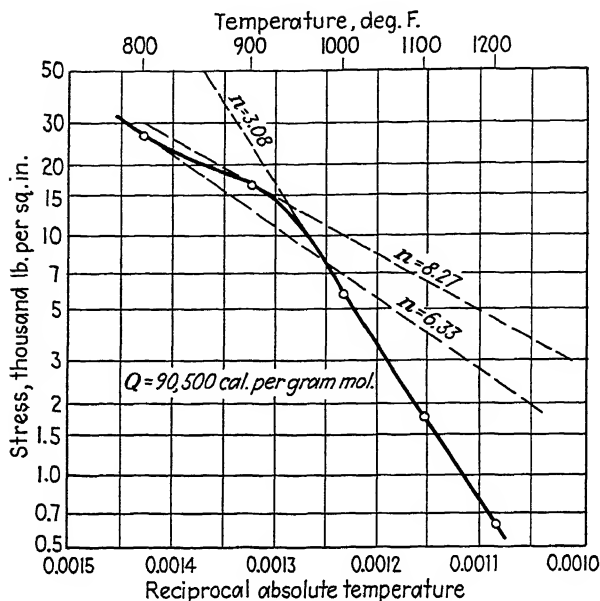
FIG. 11.—ELECTRIC-FURNACE KILLED 0.15 PER CENT C STEEL TESTED BY CLARK AND WHITE.   (1 PER CENT IN 10,000 HR. CREEP STRESS.)
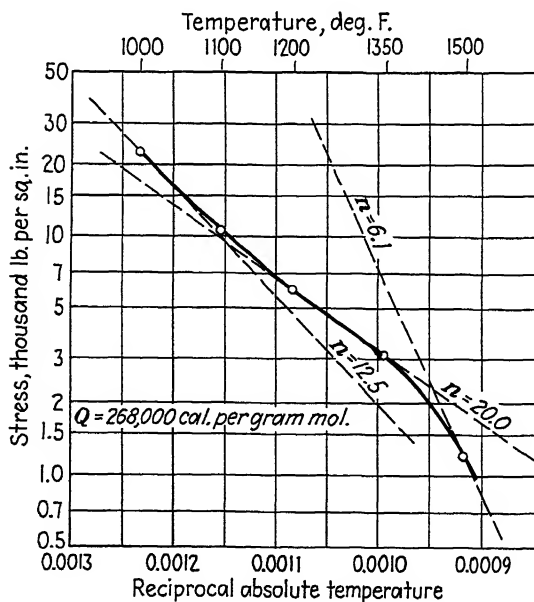
FIG. 12.—AUSTENITIC STEEL TESTED BY F. H. NORTON: 19 PER CENT NI, 6 PER CENT CR, 1 PER CENT SI.   (1 PER CENT IN 10,000 HR. CREEP STRESS.)

creep of metals, as pointed out by Dr. Condon.   The essential difference between the two problems lies in the eligibility concept.   Whereas all molecules of a fluid have equal chances of migrating under shear, the case is different with crystalline aggregates, where crystalline restraints admit only certain "eligible regions" to the chance of migration.   The application of an adaptation of the Eyring theory to the creep problem, which Dr. Condon proposes to present, promises to be a most welcome contribution.

Before a completely acceptable theory of the energetics of creep is achieved, it will be necessary, as Dr. Sturm's discussion brings out, to take into account the part of curve where creep takes place at a gradually decreasing rate and approaches a zero rate.   A range of temperature is found for each metal and alloy, however, above which a rather constant rate of creep may be observed over a considerable interval. In such instances, viscous boundary flow of material seems to have a predominating influence above that of slip in contributing to creep deformation, and the reaction rate with which we are concerned is to be associated largely with this viscous boundary flow.   At the so-called strain-hardening temperature, viscous boundary flow is of less relative importance than slip; nevertheless, creep occurring under these circumstances involves an activation of the boundary material associated with crystallite formation.   The activation energy of creep, however, when derived from data below or above the so-called equicohesive or recrystallization temperature, appears to be of approximately the same magnitude if the analysis behind Figs. 11 and 12 can be accepted.

The plastic gliding of crystals, referred to by Mr. Orowan in his discussion, is under all circumstances to be regarded as a component of creep strain, whether one deals with the primary or secondary stages.   The relative contributions of plastic gliding (slip) and viscous flow at the grain boundaries of the crystal aggregate, compared to the measured permanent deformation, vary widely with the mode by which this deformation is produced.   It has been convenient, as a matter of practical definition, to consider creep as the very slow and often uniform rate of deformation, for which the evidence indicates that the viscous boundary flow is predominately large.   Rapid time-to-rupture tests, as shown in Fig. 7 of Mr. Parker's discussion, indicate that the same general type of equations apply to the relation between stress, time and load as established for slow tests.   The Becker formula, to which Mr. Orowan refers, does not fairly depict the facts of these deformations, whether it be applied to data involving the rate of plastic gliding of crystals or to viscous movements of crystals.   It is not entirely clear that any essential difference exists in the crystal gliding whether it contributes to primary creep or furnishes the principal mode of deformation in secondary creep.   In either case, the Becker formula does not seem to satisfactorily correlate the measurements.

It was not the intention to convey an idea that atomic rearrangements or self-diffusion cannot take place below the recrystallization temperature and promote creep, as Mr. Orowan has gathered.   The increasing formation of viscous boundary material, accompanying crystallite formation as deformation proceeds below the recrystallization temperature, should merely be expected to vary the net concentration of regions "eligible" for thermal rearrangements in a different degree than obtains at the higher temperatures where the condition of the grain-boundary material is predominant in determining the creep characteristics.

Mr. Orowan inquires as to why there is a tremendous number of papers dealing with this subject presenting a complexity of views and not more straightforward explanation in terms of the laws of deformation to be learned from single crystals. While it is not the remotest intention of the author to disparage the great importance of single-crystal studies and the light of fundamental information that such studies promise, it should not be forgotten that the primary industrial interest prompting

its expenditures upon creep studies has been to obtain directly applicable engineering data upon commercial materials. Such expenditures of efforts and funds continue in what seems to be an endless and tedious investigation of new metals and alloys for high-temperature service, which make their appearance more rapidly than their creep characteristics can adequately be determined. Any generalization and rationalization of the laws governing the creep of metals that may point the way to "short-cuts" in reliably determining the information that industry so eagerly desires, is of value no matter how crudely formulated from the point of view of one interested in the fundamentals of deformation in single crystals. As for the paper under discussion, the writer believes that it represents the first practical attempt to draw attention to certain possibilities in the generalization of the temperature coefficients of creep rates. If this paper serves in any degree to focus attention upon such possibilities, which may eventually lead to a theoretical development of creep laws that eliminates the number of temperature points necessary to establish data usable over a range of temperature, it will have served a practical end.

Effect of Silicon on Chromium-molybdenum Steels for High-temperature Service, with a Note on the Effect of Copper

BY H. D. NEWELL*

THERE has been much research and commercial development in recent years in the use of chromium and nickel in steels of various types, including those intended for high-temperature service. By "high-temperature steels" are meant those specifically designed for service at elevated temperatures in steam plants, oil refineries and other industries where high-temperature operations are conducted. This paper is devoted to some preliminary data on the effect of silicon on certain of the most popular chromium-molybdenum steels now being used in quantity by the refining industry and includes a short statement on the influence of copper in steels intended for high-temperature service.

USES OF SILICON

Next to oxygen, silicon is the most widely distributed and abundant of the earth's substances. Although classed as a nonmetal, it is highly important in the metallurgy of all steels, having been used for years as an efficient and economical degasifier and deoxidizer. Silicon is added to various steels in the form of ferrosilicon, generally at the end of the heat so as to avoid oxidation losses. With acid steels it is added in the furnace (also in the ladle) and generally with basic steels is added in the ladle, so as to avoid reaction with the basic lining through high-temperature acidic reaction with silica, which may be formed by oxidation of the silicon alloy. Several grades of ferrosilicon are available, containing, respectively, 15, 50, 75 and 90 per cent Si. By far the largest tonnage produced is the 50 per cent grade although the 75 and 90 per cent ferrosilicons are used as ladle and furnace additions in the manufacture of steels of high silicon content.

The introduction of silicon into steel as an alloying element is well known in connection with high-yield-strength constructional steel for bridges, ships, car construction, etc., and it is also well known as an alloy-

ing element in electrical sheet steel and in silicon-manganese spring steels. Smaller amounts of special silicon-containing alloys are made for specific applications such as the high silicon acid-resistant cast irons, alloys high in chromium-nickel and silicon for high-temperature and corrosion-resistant uses, and chromium-silicon steels for exhaust valves of internal-combustion motors.   In the last mentioned application, silicon is added for its specific action in enhancing resistance to scaling.

Action of Silicon when Added to Relatively Pure Iron

Silicon has a density of 2.4 grams per cubic centimeter compared with 7.84 grams per cubic centimeters for pure iron.   A small addition of silicon by weight, therefore, means a relatively large addition by volume. Silicon does not form a true carbide in steel and simply goes into solution in the ferrite.   According to Corson,[1] iron-silicon alloys up to 14.3 per cent Si are of alpha solid solution type with silicon dissolved in the solvent iron.   (Certain irregularities in properties, crystal lattice constant, etc., occur below 14.3 per cent Si and these are more or less anomalies when contrasted to true alpha solid solutions.)   Silicon reduces air hardenability, increases transformation temperatures and hardness in the annealed state as the percentage of silicon increases.   The introduction of silicon into iron causes a decrease in density and conversely an increase in specific volume.   It increases specific heat and electrical resistance and has decided indirect effects on other electrical characteristics.   Many investigations show that silicon lowers the solubility of carbon in iron.   We are not here concerned with these effects but mainly with changes in mechanical properties, creep strength, corrosion resistance and oxidation resistance, as is pertinent to suitability for high-temperature application.

It has been known for a long period that silicon increases the hardness and brittleness of iron.   After a survey of the literature, Greiner, March and Stoughton[2] stated that silicon increases the strength (room temperature) of iron-silicon alloys nearly linearly to at least 4 per cent Si, beyond which a sharp decline occurs.   Further, the ductility beyond 2 per cent Si is low.   Yensen's[3] work on vacuum-melted iron-silicon alloys is perhaps the most complete in existence and his curve for the strength properties of annealed iron-silicon alloys is reproduced in Fig. 1.   An unexplained minimum in properties occurs at about 2.50 per cent Si but otherwise both tensile strength and yield point increase in practically straight-line functions.   The corrosion-test results summarized in the recent book on Alloys of Iron and Silicon[1] indicate no appreciable increase in corrosion resistance in iron-silicon alloys under atmospheric corrosion, hot and cold aerated water or under mineral acids until a critical silicon content approaching 13 per cent is reached, whereupon a decided increase

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[1] References are at the end of the paper.

in resistance to corrosion by mineral acids occurs.   Generally speaking, not enough data are available to indicate whether silicon has a beneficial effect when present in nominal amounts; i.e., 3 per cent or less.

In common with chromium, silicon has the power to form hard, dense refractory surface oxides, therefore its addition to iron alloys results in an improvement in resistance to oxidation.   Its use in this connection
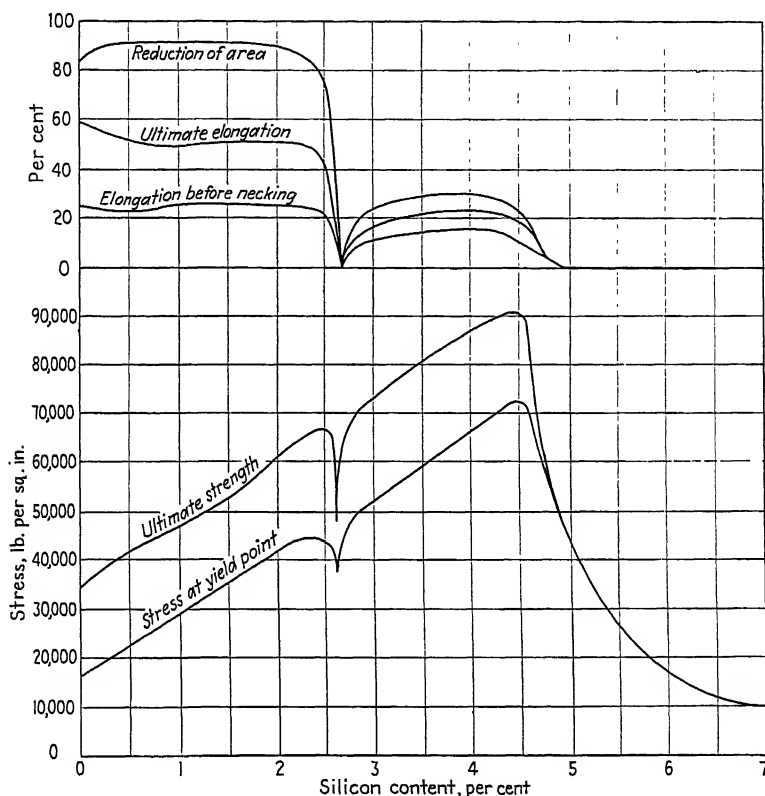
FIG. 1.—MECHANICAL PROPERTIES OF IRON-SILICON ALLOYS MELTED IN VACUO. ANNEALED.   (*After Yensen.*)

is exemplified in the well-known chromium-silicon automotive valve steels. Two steels in wide use for this purpose are the 2 per cent Cr, 3 per cent Si steel and the 9.5 per cent Cr, 3 per cent Si alloy.   These steels contain approximately 0.40 per cent C, are quite brittle in the cold and are of relatively low strength at elevated temperature.   They do, however, offer excellent resistance to high-temperature oxidation as encountered in the exhaust valves of gasoline engines.

Steel containing 2 to 3 per cent Si with low carbon has been noted as having good resistance to water vapor at high temperature[4] and Pfeil,[5] investigating the oxidation resistance of various steels, found that the

outer layers of scale on 2 per cent Si steel contained only traces of silicon whereas the inner layer contained more than 4 per cent Si. This may be interpreted as meaning that a concentration of silicon or silica at the scale-metal interface retards oxygen diffusion and hence oxidation of the metal.

In the higher alloy steels such as 18-8, the addition of 2 per cent Si greatly retards the attack of sulphur-bearing flue gases. For this reason, such material was employed in the superheater tubes of the Detroit-Edison high-temperature steam superheater.[1] The installation has operated three years or more at steam temperatures up to 1100 °F., with
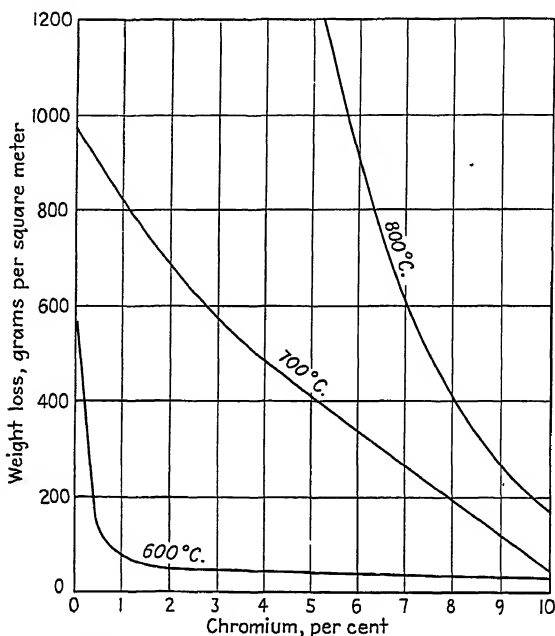
FIG. 2.—SCALING EXPERIMENTS ON CHROMIUM STEELS AT DIFFERENT TEMPERATURES.
(*After Jungbluth and Muller.*)

no sign of external (or internal) attack. Plain 18-8 in flue gases from the burning of fuel oil containing 1.5 per cent S has shown rapid attack in test work at metal temperatures above 1200°F., also where sludge acid fuel is burned. There seems to be no dearth of evidence that silicon additions retard the oxidation rate of steels in oxidizing atmospheres and burned gases at elevated temperatures.

Jungbluth and Muller,[6] investigated the properties of low-cost heat and corrosion-resistant steels for steam-boiler construction. The investigation is of particular interest because it deals with chromium-molybdenum steels containing from about 1 to 6 per cent Cr, such as are finding wide application in this country in oil refineries and steam superheater construction.

The creep properties of a large group of steels, including several molybdenum and chromium-molybdenum steels, were investigated roughly by weighting wires (rods) and subjecting them to uniform heating to determine those resistant to sagging.   Of the steels selected for fur-
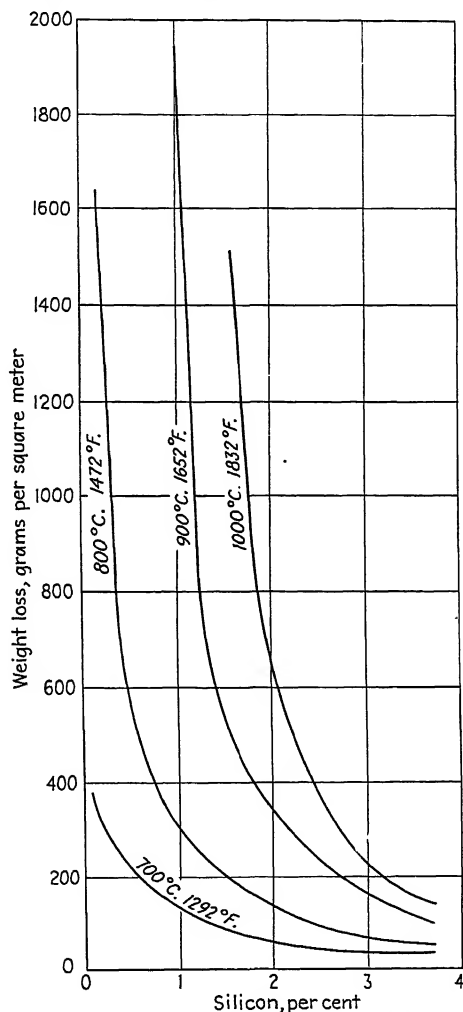
Fig. 3.—Effect of silicon on scaling resistance of a 6 per cent Cr, 0.50 per cent Mo, 0.50 per cent V steel.   (*After Jungbluth and Muller.*)

ther testing, carbon-molybdenum and chromium-molybdenum steels were outstanding.   The steels showing the best properties were subjected to additional testing, which included creep tests, short-time high-temperature tests, oxidation-resistance tests and ability to be fabricated into seamless tubing.   Fig. 2 is reproduced from this work to show the influence of chromium on resistance to oxidation at various temperatures.

The tests were of 120 hr. duration. Attempts were also made to substitute silicon in part for chromium to improve oxidation resistance at lower cost than if chromium alone were used. The value of silicon in this respect may be noted in Fig. 3, which shows resistance to scaling imparted by various silicon contents when added to 6.0 per cent chromium-molybdenum-vanadium steel. Aluminum was not considered a successful substitute for chromium because of difficulties encountered in the manufacture of the high-aluminum steels and because of the tendency of such steel to nitride in certain services. Aluminum, however, improved oxidation resistance markedly. The investigation resulted in establishment of several commercial grades now sold by the Krupp company of low-chromium-molybdenum (1 per cent Cr) and 6 per cent chromium-molybdenum steel with or without silicon. Incidentally, the lower chromium alloys were found to be superior in creep strength to the 6 per cent Cr alloys but had inferior oxidation resistance, as might be expected.

American metallurgists have been rather slow to take advantage of the economic possibilities of adding silicon to high-temperature steels although several steels of this type are now on the market. This situation is due no doubt to several factors, among which may be mentioned: (1) lack of accurate data concerning the effect of silicon on mechanical properties and creep strength, (2) difficulty from the manufacturer's point of view in handling steels containing 1.50 per cent or more silicon and (3) the fear that silicon will contribute to brittleness and unreliability in service. Competition with other elements such as titanium and columbium, which retard air-hardening properties and enhance resistance to scaling, has also been a factor.

The remainder of this article attempts to supply information, admittedly incomplete, on the effect of silicon in 2 per cent Cr, 0.50 per cent Mo and 5 per cent Cr, 0.50 per cent Mo steels.

EXPERIMENTAL WORK

A laboratory study of the effect of silicon in various amounts in 2 per cent Cr, 0.50 per cent Mo steel was made in the author's laboratory by melting a series of induction-furnace melts ranging from 0.20 to 3.00 per cent Si in graduated steps. In addition, two melts of 5 per cent Cr, 0.50 per cent Mo steel with approximately 1.5 per cent Si were prepared. Analysis of the experimental alloys is given in Table 1.

Mechanical properties of 1-in. round after a complete soft-annealing treatment were as shown in Table 2. It may be noted here that silicon gradually stiffens the metal, causing an increase in tensile strength, yield point and Brinell hardness with a corresponding drop in ductile properties. Similar data on physical properties, annealed, are also given for the two experimental heats of 5 per cent Cr, 0.60 per cent Mo alloys with high silicon content, together with properties for the usual commercial alloy

containing 0.50 per cent maximum silicon. These data are also given in Table 2.

TABLE 1.—*Chemical Composition of Experimental Alloys*

Heat No.	Composition, Per Cent				
	Carbon	Manganese	Silicon	Chromium	Molybdenum
2 PER CENT CHROMIUM, 0.50 PER CENT MOLYBDENUM SERIES					
849	0 11	0.30	0.20	1.79	0.61
898	0.12	0.44	0.55	1.98	0.53
900	0.13	0.57	1.02	2.02	0.54
899	0.16	0.56	1.22	2.06	0.54
910	0.13	0.52	1.93	1.94	0.59
911	0.13	0.59	2.96	1.94	0.53
5 PER CENT CHROMIUM, 0.50 PER CENT MOLYBDENUM SERIES					
873	0.14	0.62	1.48	5.57	0.68
874	0.11	0.60	1.60	5.39	0.61
Commercial..	0.16	0.36	0.37	5.13	0.58

TABLE 2.—*Physical Properties of One-inch Round after Full Annealing*

Heat No.	Silicon Content, Per Cent	Ultimate Strength, Lb. per Sq. In.	Yield Point, Lb. per Sq. In.[b]	Propor-tional Limit, Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Reduction, Per Cent	Brinell Hard-ness
2 PER CENT CHROMIUM, 0.50 PER CENT MOLYBDENUM SERIES[a]							
849	0.20	66,350	39,100		36.5	63.0	125
898	0.55	71,500	40,500	30,500	35.0	68.2	131
900	1.03	86,680	47,280	35,000	32.5	67.3	156
899	1.22	89,500	48,750	40,000	29.0	64.0	170
910	1.93	90,370	58,408	42,500	31.0	65.9	179
911	2.96	96,455	63,630	47,975	28.0	51.9	207
5 PER CENT CHROMIUM, 0.50 PER CENT MOLYBDENUM SERIES[a]							
873	1.48	88,420	43,080	33,000	32.5	65.2	197
874	1.60	87,500	56,000	46,500	34.0	73.0	170
Commercial.	0.37	75,950	31,400	26,500	33.5	69.3	143

[a] Average value of two tests.

[b] Yield-strength values obtained by the offset method and values shown are for stresses at permanent set of 0.1 per cent of original gauge length.

Figs. 4 and 5 show, respectively, the influence of increasing silicon content on physical properties of 2 per cent Cr, 0.50 per cent Mo steel

and typical stress-strain diagrams giving experimental values for proportional limit and moduli of elasticity.   Impact strength at room temperature, plus 25° F., and minus 25° F., is given in Table 3.

Increased silicon influences the·properties of the 5 per cent Cr type steel in much the same way as when added to the 2 per cent Cr alloy. The tensile, yield and hardness are increased and impact apparently suffers more in the 5 per cent Cr steels than in the alloy with less chro-
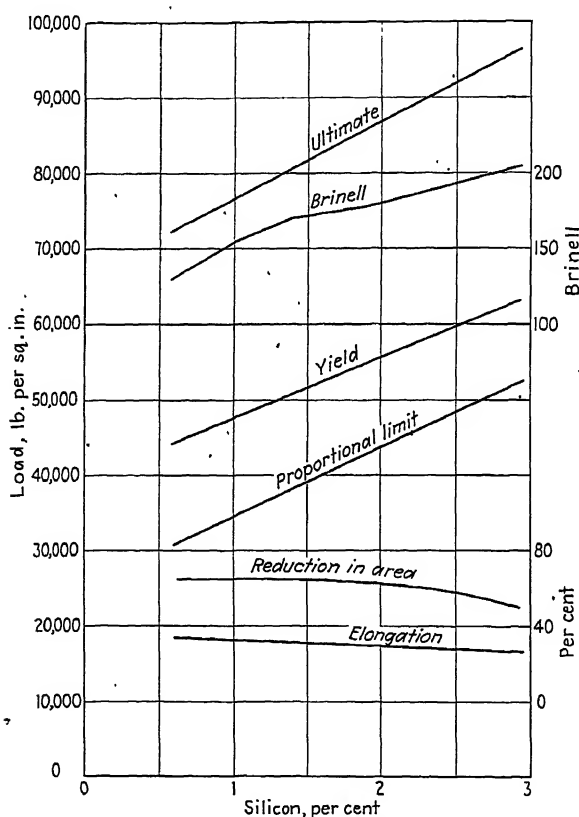
Fig. 4.—Effect of silicon on room-temperature physical properties of 2 per cent Cr, 0.50 per cent Mo steels.

mium.   Small variations in carbon have a decided effect with the lower carbon alloy, exhibiting the better impact properties.   The properties of a 5 per cent chromium-molybdenum steel with higher silicon, namely, 2.5 per cent, are disappointing in so far as tube fabrication is concerned. Such an alloy has excellent scale resistance and may be hot-worked satisfactorily, but is extremely brittle in the cold state.   While it might be adaptable for certain heat-resistant purposes, it is too fragile for application in boilers or as refinery tubes, which are subject to shock stresses.

This is becoming apparent in the 1.50 per cent Si alloy, as evidenced by the low impact values obtained in the experimental alloy containing
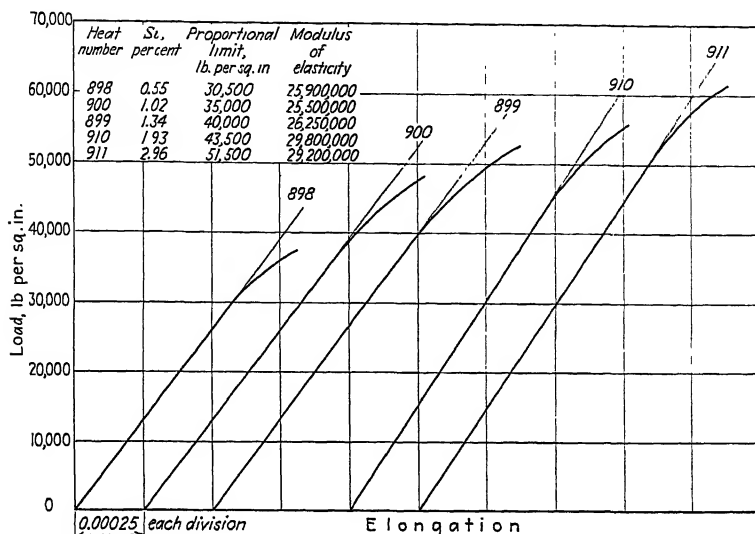
FIG. 5.—STRESS-STRAIN DIAGRAM SHOWING INFLUENCE OF SILICON ON PROPORTIONAL LIMIT OF 2 PER CENT CR, 0.50 PER CENT MO STEEL.

TABLE 3.—*Impact Value, One-inch Round Annealed*
CHARPY FOOT-POUNDS

Heat No.	Silicon, Per Cent	Room Temperature, Deg. F.	Plus 25° F.	Minus 25° F.
2 PER CENT CHROMIUM, 0.50 PER CENT MOLYBDENUM SERIES				
849	0.20	61.0	60.0	54.0
898	0.55	39.0	39.5	30.0
900	1.03	44.0	41.5	39.0
899	1.22	42.0	44.0	39.0
910	1.93	33.0	36.0	8.0
911	2.96	2.0	3.5	1.0
5 PER CENT CHROMIUM, 0.50 PER CENT MOLYBDENUM SERIES				
873	1.48	10.0		
874	1.60	35.5		
Commercial......	0.37	55.0		

* Average of three tests.   Specimen 0.394 in. square, drilled notch.

0.14 per cent C. It seems indicated that carbon content in the 5 per cent Cr alloy should be 0.10 per cent, or possibly 0.12 per cent maximum, to avoid this condition.

SHORT-TIME TENSILE PROPERTIES

The short-time test is not a reliable criterion for judging the ability of the metal to resist stress for long periods of time at high temperature, but such tests are interesting in developing information on the influence
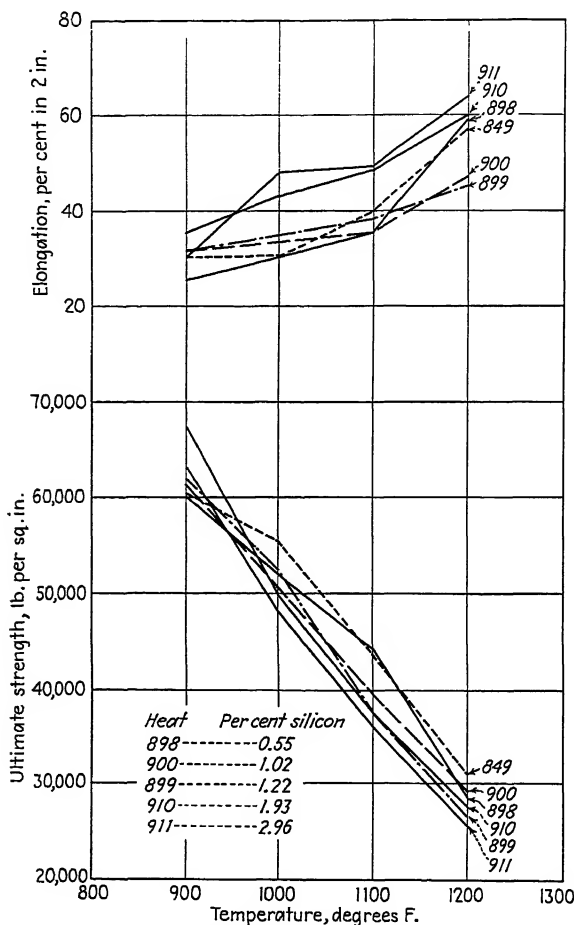
FIG. 6.—EFFECT OF SILICON ON SHORT-TIME TENSILE PROPERTIES OF 2 PER CENT CR, 0.50 PER CENT MO STEELS.

of various elements on mechanical properties, and they have some significance in indicating how a steel will behave under sudden stress such as might be encountered under sudden pressure increase or when hot spots develop in refinery tubes because of coking and irregular furnace conditions. Short-time tests have been made on the 2 per cent Cr steels with various silicon contents. Under standardized test conditions, the influence of silicon is as shown in Fig. 6. The individual heats were

soft-annealed prior to test and for this reason it is interesting to note that silicon has no pronounced effect on short-time strength up to at least 1200° F.; in fact, the alloys with higher silicon contents show the lowest strength properties between about 950° and 1200° F. At 900° F., the effect of silicon in stiffening the ferrite is noticeable, and at this tempera-
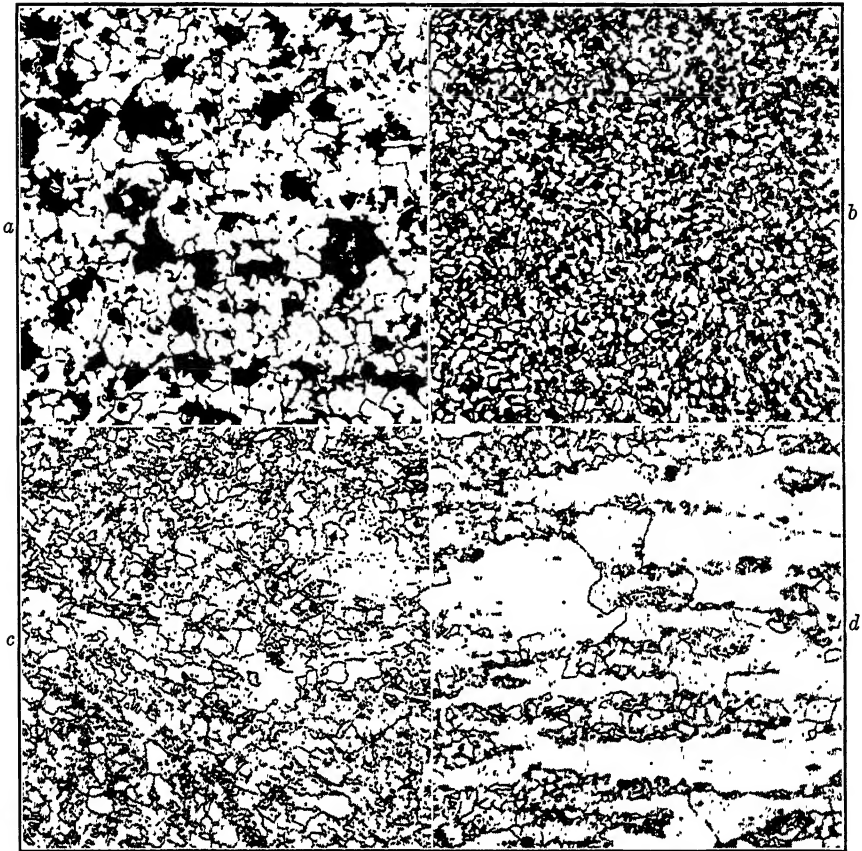
FIG. 7.—MICROSTRUCTURE OF 2 PER CENT CR, 0.50 PER CENT MO, ALLOYS WITH VARIOUS SILICON CONTENTS. ANNEALED. × 100.

a, 0.55 per cent Si. c, 1.93 per cent Si.
b, 1.22 per cent Si. d, 2.96 per cent Si.

ture, the higher silicon alloys show a slight superiority over those of lower silicon content. At high temperatures—i.e., within the working or rolling range, silicon in amounts of one per cent or more seems to cause softening, and in this connection it has been observed that certain high-silicon steels have excellent elongation through the working range but are easily guide-marked or roll-marked during the rolling of tubes or other products.

The microstructures of several of the 2 per cent Cr steels, as annealed, are illustrated in Fig. 7. A decided tendency toward coarse grain structure may be noted in the alloy containing 2.96 per cent Si, and this is reflected in the impact properties shown for this composition.

CREEP PROPERTIES

There are no data available at this time that accurately indicate the effect of silicon variation on the creep strength of chromium-containing steels. Doubtless silicon has an appreciable effect, considering that it enters solution in the ferrite and also tends to alter the form of the carbides. Slight changes of chromium also affect the condition of the carbide in that as chromium content increases, the carbide changes in annealed steels from pearlitic form to spheroidized form. This makes it necessary to compare creep-strength properties of constant chromium-content alloys of variable silicon content before definite statements can be made.

Generally speaking, silicon seems to aid resistance to creep of steel alloys up to about 950° F., above which available data seem to indicate that silicon in increasing amounts depreciates creep resistance. The many factors affecting the creep properties of steel, such as melting and casting practice, inherent grain size, composition, heat-treatment, and so on, make for difficulty in determining the true effect of any given element. Clark and White[8] have described these factors and state that preliminary results indicate that silicon additions in excess of a given amount do lower creep resistance. Their article also makes possible a comparison of carbon-molybdenum steels containing high and low silicon.

TABLE 4.—*Clark and White's Data*

Alloy	Chemical Composition, Per Cent	Temperature, Deg. F.	Rate of Creep per 1000 Hr.	
			0.01 Per Cent	0.10 Per Cent
1	C, 0.16, Si, 0.23, Mo, 0.42...............	800	15,500	26,000
2	C, 0.11, Si, 1.35, Mo, 0.50...............	800	18,000	29,000
1	As above............................	1000	10,700	17,800
2	As above............................	1000	5,000	9,200
1	As above............................	1200	480	2,000
2	As above............................	1200	720	1,850

The data in Table 4 are abstracted from Clark and White's Table 1. These data indicate that the high-silicon alloy is superior at 800° F., but inferior to the low-silicon alloy at the higher temperatures. Other data

have been compared by the author and, allowing for the effect of small differences in chromium content of several alloy steels, those containing the higher silicon contents show the lowest creep-strength properties. Therefore, until information to the contrary is available it can be inferred that silicon additions in excess of a normal amount for deoxidation purposes, or perhaps slightly more, tend to reduce creep strength at the higher temperatures.

OXIDATION RESISTANCE

The most beneficial action of silicon lies in its ability to improve resistance to scaling at high temperature. The value of increasing silicon
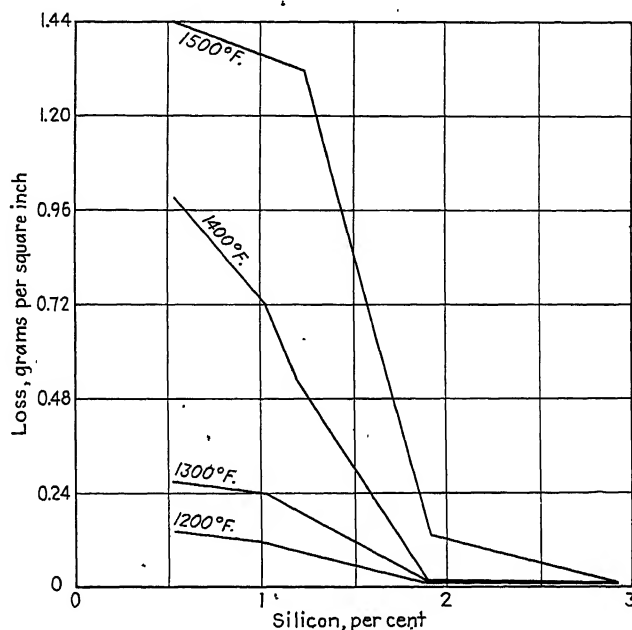
FIG. 8.—EFFECT OF SILICON ON SCALING RESISTANCE OF 2 PER CENT CR, 0.50 PER CENT MO, 0.16 PER CENT C, STEEL.

content in this direction may be noted in Fig. 8, which shows results of oxidation tests of 100 hr. duration performed by heating in an oxidizing atmosphere in an electric muffle furnace. Scale loss is reported in grams per square inch and all samples were of equal exposed surface area.

SUMMARY

Where oxidation resistance is of prime importance, improvement in this direction can be gained at low cost, by adding silicon to the chromium-molybdenum high-temperature steels. Until further data are available, silicon should be limited to about 1.50 per cent in steels containing 2 to

5 per cent Cr.   Higher silicon results in loss of impact strength and tends to reduce ductility; and should be avoided where shock stresses are likely to be encountered when the metal is cold.

The increased resistance to oxidation is gained at some sacrifice in high-temperature strength properties (both short-time and creep strength) and it is believed further data will bear out this contention.   A compromise must be made in using the silicon-containing alloys, and the choice of material will be dependent on whether maximum creep strength or maximum oxidation resistance is of paramount importance.

NOTE ON EFFECT OF COPPER

Copper in small amounts improves the resistance of steel to dilute acid solutions of a reducing character and also its resistance to atmospheric corrosion.   The limited solubility of copper in iron makes it of use in constructional steels where advantage is taken of a precipitation-hardening reaction to cause increase in yield strength.   It also is stated by certain investigators that copper improves resistance toward oxidation; the influence on oxidation resistance is slight, however.   Copper is non-resistant to sulphur compounds at elevated temperatures; consequently, it has not been used in steels for high-temperature service.   The lack of resistance of copper-bearing steel to corrosion is confirmed by Egloff and Morrell,[9] who report results of a corrosion test covering a period of 20 days with cracking oil containing 1 per cent S at 460° C. (860° F.). The samples tested were suspended in the vapor zone of the reaction chamber.   The copper-bearing steel lost more than plain steel, therefore did not show promise for this service.   The reactivity of copper and sulphur at elevated temperature would lead one to suspect such a result and, in consequence, copper additions have been avoided in high-temperature steels.

An exception to this lies in the use of copper-steel boiler tubes for nominal temperature conditions where corrosion from boiler waters of poor quality is to be combated.   In this case, the copper-bearing steels are not subjected to temperatures in excess of about 450° F., and they are not called upon to resist the highly corrosive effect of oil products containing appreciable quantities of sulphur.

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DISCUSSION

C. L. CLARK,* Ann Arbor, Mich. (written discussion).—Silicon is an element that has received too little attention, in so far as its influence upon the high-temperature properties is concerned, and when the true value of this element is recognized it will be present in relatively large amounts in the majority of steels used for high-temperature service. In fact, this trend is already occurring, as many of the higher silicon steels are now finding wide commercial applications.

TABLE 5.—*Comparative Tensile Properties*
Two 4–6 Cr + Mo Steels Containing 0.18 and 1.55 Per Cent Si

Tempera-ture, Deg. F.	Silicon, Per Cent	Tensile Strength, Lb. per Sq. In.	Yield Stress, Lb. per Sq. In.		Proportional Limit, Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Reduction of Area, Per Cent
			0.1 Per Cent	0.2 Per Cent			
85	0.18	66,575	25,400	26,250	19,000	39.0	80.5
	1.55	82,100	45,000	45,000	36,250	38.8	76.2
1000	0.18	44,465	16,750	17,300	7,500	28.5	73.5
	1.55	45,500	24,250	25,625	15,000	42.75	83.6
1100	0.18	34,375	14,900	15,400	6,000	38.75	87.3
	1.55	33,575	18,000	20,250	8,000	58.5	89.95
1200	0.18	25,800	11,000	11,300	1,500	46.0	91.0
	1.55	24,000	13,750	15,000	5,500	70.75	93.65
1300	0.18	19,000	8,650	9,500		65.0	94.55
	1.55	15,000	9,000	10,000		79.0	95.65
1400	0.18	13,275	6,500	7,250		65.0	95.9
	1.55	10,340	4,875	5,750		101.0	97.6

While we are in general agreement with the results presented it is believed that greater consideration should perhaps be given to certain of the points raised. Our laboratories have done considerable work on several of the steels herein considered, and since all of our results were obtained from standard commercial heats, rather than from small induction ones, a comparison will be valuable in indicating whether or

* Research Engineer, College of Engineering, University of Michigan.

not the same trends exist.   This discussion will be largely confined to two representative steels, 4–6 Cr + Mo with 0.18 and 1.55 per cent Si.

Tensile Properties.—In so far as the short-time tensile properties at room and elevated temperatures are concerned, we have likewise found increased silicon content to improve the strength characteristics at room temperature and to slightly lower the tensile strength, but not the yield stress or proportional limit, at the elevated temperatures.   The increased silicon content does, however, greatly increase the ductility at the elevated temperatures and we believe this to be of considerable importance.   The tensile properties of these two steels are summarized in Table 5.

TABLE 6.—*Comparative High-temperature Impact Characteristics*
Two 4–6 Cr + Mo Steels Containing 0.18 and 1.55 Per Cent Si

Temperature, Deg. F.	Silicon, Per Cent	Charpy Impact, Ft.-lb., after Designated Holding Times	
		1 Hr.	1000 Hr.
80	0.18	81.3	
	1.55	69.3	
500	0.18	68.7	77.0
	1.55		
600	0.18	72.5	80.5
	1.55		
750	0.18	75.0	73 3
	1.55		
900	0.18	64.5	52.0
	1.55		
1000	0.18	58.7	61.0
	1.55	59.0	53.0
1100	0.18	54.3	56.0
	1.55	56.0	56.0
1200	0.18	53.7	40.0
	1.55	51.0	45.5
1300	0.18		
	1.55	50.0	45.5
1400	0.18		
	1.55	46.5	44.0
1500	0.18		
	1.55	42.5	34.5

Impact Resistance.—Likewise, in connection with impact resistance, it was found that the increased silicon content lowered the room-temperature values to a slight

extent but had no detrimental influence on the resistance at the elevated temperatures. In fact the results, given in Table 6, show the high-silicon type to have good resistance to impact after exposure times of 1000 hr. at temperatures as high as 1500° F.

Creep Characteristics.—A casual review of the present paper might lead to the conclusion that increased silicon content decreases the creep resistance under all conditions. Such however is not believed to be true and the data presented in Table 4 indicate that this occurs only at certain intermediate temperatures; in other words, at the lower temperatures increased silicon improves the creep resistance and the same is likewise true to a lesser degree at the more elevated temperatures.

The creep characteristics of the two 4–6 Cr + Mo steels being considered are shown in Fig. 9. It is apparent that at temperatures of 1000° and 1100° F. an increase in the silicon content from 0.18 to 1.55 per cent has reduced the creep strength to some extent, but at 1200° F. it has been slightly beneficial and the shapes of the two curves indicate that it would be even more so at the more elevated temperatures.

The question now arises as to the temperatures at which the higher creep resistance is of the greater importance. For cracking tubes for oil-refinery service it is generally
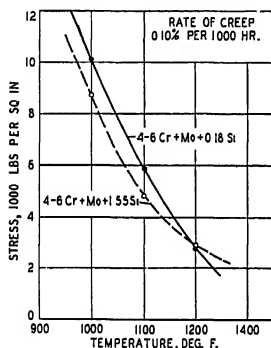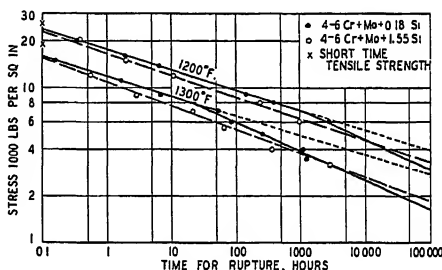
FIG. 9. FIG. 10.

FIG. 9.—CREEP CHARACTERISTICS OF 4–6 PER CENT CR + MO STEEL CONTAINING 0.18 AND 1.55 PER CENT SI.

FIG. 10.—STRESS-RUPTURE CHARACTERISTICS AT 1200° AND 1300° F. OF TWO CR + MO STEELS CONTAINING 0.18 AND 1.55 PER CENT SI.

agreed that the greater creep resistance is required at the temperatures encountered during the latter part of the operating cycle, which may be considerably above the normal operating temperatures. Under these conditions an increase in the silicon content of the 4–6 Cr + Mo steel to 1.50 per cent would be advantageous rather than detrimental, in so far as the creep resistance is concerned under operating conditions.

Rupture Strength.—While this subject was not discussed in the paper, the results obtained from stress-rupture tests are believed to afford a valuable means for comparing various steels. As shown in previous papers,[10,11] tests of this type are believed to be of great importance because the results are dependent not only on the strength or load-carrying ability of the steel but upon its surface and structural stability as well. Furthermore, the fractured specimens give the ductility up to rupture and thus indicate the degree of deformation the steel will undergo before actual failure occurs.

Fig. 10 is included as representative of the influence of an increase in silicon content on the stress-rupture characteristics at 1200° and 1300° F. For the higher silicon steel,

[10] Fracture of Carbon Steels at Elevated Temperatures. *Trans.* Amer. Soc. Metals (1937), **25**, 863–885.

[11] Rupture Strength of Steels at Elevated Temperatures. A.S.M., 1937 Convention.

the results are expressible by a single line at each of the two temperatures, and this is an indication of the high surface stability.   With the lower silicon steel a break occurs in this straight-line relationship, thus indicating that pronounced oxidation has occurred.

For the shorter fracture times the lower silicon steel possesses a greater rupture strength than the higher silicon modification.   For the more prolonged times, however, this condition is reversed, thus again indicating the advisability of a higher silicon content for service at these more elevated temperatures.

Fig. 11 sets forth the ductility characteristics of the fractured specimens at 1200° F. and shows that the ductility of the higher silicon modification remains practically constant as the fracture time is extended from a few minutes to 1000 hours.   With the standard 4–6 Cr + Mo steel, however, a marked decrease occurs in the ductility with increasing fracture times.   This again shows the greater stability, both with respect
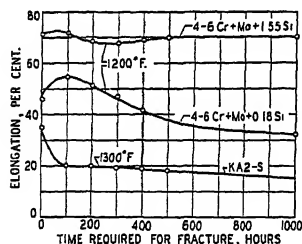
Fig. 11.

Fig. 12.

Fig. 11.—Influence of time at 1200° F. on ductility characteristics of two 4–6 Cr + Mo steels containing 0.18 and 1.55 per cent Si.
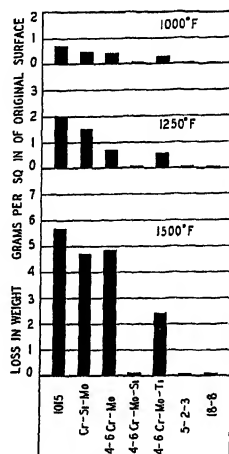
Fig. 12.—Comparative oxidation resistance of designated steels at indicated temperatures.

to surface and structure, of the higher silicon steel and indicates that it would deform to a considerably greater extent before actual failure occurred.

Oxidation Resistance.—The greatly improved resistance to oxidation imparted by an increased silicon content is illustrated in Fig. 12.   Even at 1500° F. the 4–6 Cr + Mo steel containing 1.50 per cent Si oxidized very little under an exposure time of 1000 hr.   In fact, under the given test conditions it compares favorably in this respect with the 18-8 steel.

Not only does the increased silicon content greatly improve the resistance to general oxidation; it also retards the intergranular oxidation that occurs in most steels at the more elevated temperatures under the combined action of stress and time. The improved resistance to both of these types of attack at 1300° F. is shown in the two photomicrographs of Fig. 13.   Even though the higher silicon steel required nearly three times as long for fracture, it shows only a very slight surface attack and no intergranular attack.   The lower silicon steel, on the other hand, possesses a relatively heavy oxide layer and considerable intergranular attack has occurred as well.

Conclusion.—It is believed that these results, together with those of the authors, clearly demonstrate the improved high-temperature characteristics that can be

obtained through the use of proper silicon additions. This element certainly increases the surface stability, with respect to oxidizing conditions, and the structural stability, and thus, indirectly perhaps, greatly improves the load-carrying ability and the ductility up to fracture, especially at the more elevated temperatures.

FIG. 13.—SURFACE OF SPECIMENS FRACTURED AT 1300° F. × 100.
a, 4–6 per cent Cr + Mo + 1.55 Si. Stress 3200 lb., 2987 hours.
b, 4–6 per cent Cr + Mo + 0.18 Si. Stress 4000 lb., 1120 hours.

MEMBER.—Did I understand from Dr. Clark that the increased silicon had a tendency to lower the grain size?

C. L. CLARK.—The microstructures of the two steels in the original annealed condition showed both to possess approximately the same grain size. After the 1300° F.

test, the grain size of the lower silicon steel had coarsened while that of the higher silicon steel had not. Provided the same general practice was followed in making both of these steels, this would indicate that the increased silicon content had decreased the tendency toward grain growth at 1300° F. under the given test conditions.

E. C. WRIGHT,* Pittsburgh, Pa.—I can only say the high-silicon steels are considerably harder. Our difficulty with them is getting them soft enough in the tube form.

R. L. WILSON, Canton, Ohio.—The two heats identified as 873 and 874 when tested at room temperature for impact strength show 10 ft-lb. and 35.5 ft-lb., respectively. There does not seem to be much in the comparative compositions of those two heats to explain such a big discrepancy. There might be some other physical feature such as perhaps grain size, or some factor that could not be controlled in the making of induction melts.

Having had some experience with high-silicon 5 Cr-Mo steels of this type as made in commercial lots, I feel it would be unfair to assume that there would be such a wide variation in the impact strength of such steels, and I have never seen room-temperature impact tests on this type as low as 10 ft-lb. annealed material.

H. D. NEWELL (written discussion).—The information given by Dr. Clark considerably augments the value of the paper.

We concur that silicon increases room-temperature physical properties and reduces tensile strength at elevated temperature. Yield stress and proportional limit at elevated temperatures are not particularly significant, as most design values are predicated on creep strength for given rates of creep or on total creep, depending on the type of structure. However, recent results obtained in our laboratory on commercial 2 per cent Cr-Mo steel, with high and low silicon contents, indicate that in this particular analysis yield strength may be depreciated as well as tensile strength by an appreciable silicon content. Results are given in Table 7.

Of practical significance, particularly in application of tubing of higher silicon alloys, is the increased yield strength and hardness brought about by solution of silicon in the ferrite. No amount of annealing will bring about comparable softness to the low-silicon alloys of otherwise equivalent analyses, with the result that tube expanding or rolling is made much more difficult and tedious. In fact, development of stronger tools with increased power will be necessary before satisfactory joints can be secured. In addition, header or seat material of higher strength than usual is required for the higher silicon alloys, so as to maintain a workable hardness difference between seat and tube.

As to increased ductility, or, more appropriately, plasticity, when hot, the higher silicon alloys exhibit this feature without doubt, as may be noted by elongation values given in short-time tensile data and in the ease with which such alloy steels guide-mark, scratch and overfill in hot-rolling operations. The last named makes commercial production of articles somewhat more difficult than is usual with the lower silicon varieties.

The usual commercial heats processed in our plant show satisfactory impact value, so that the original laboratory melts explored by us may have been influenced by method of melting or deoxidation. It is believed necessary to restrict silicon and regulate carbon content so as to avoid getting into alpha-delta type steels having no transformations or only minor ones, otherwise impact value may be seriously affected. Too high a carbon content may also be detrimental. Impact values given by Dr. Clark in Table 6 may be considered quite satisfactory.

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* Chief Metallurgist, National Tube Co.

As to creep properties, steels in the classification under discussion are not ordinarily used under high stress or pressure conditions at temperatures exceeding about 1200° F., because of strength limitations. In properly operated apparatus, where temperatures are more or less closely controlled, the higher strength lower silicon alloys might be the preferred form of alloy. This would be true in most cracking-still operations and in steam superheaters; in the latter, metal temperatures rarely exceed 1050° F. Under conditions of poor temperature control, excessive coking in still tubes or in superheater tubes not receiving sufficient steam flow to keep temperatures at a normal point, the increased plasticity of the higher silicon variety might carry the member through the period of overheating without rupture occurring because of low ductility in the overheat range of temperature. In numerous failures of tubes examined by the writer over a period of years, true creep failures are only rarely encountered while numerous failures of relatively short-time variety have been noted. Such failures usually exhibit considerable scaling with deformation in the form of a bulge at the hottest area. Under these conditions good rupture strength combined with additional oxidation resistance might be important.

TABLE 7

Analysis	C	Mn	S	P	Si	Cr	Mo
A	0.13	0.46	0.014	0.012	0.37	2.32	1 01
B	0.13	0.41	0.015	0.020	1.65	2 17	0.92

A

Test	Room Temperature	1000° F.	1100° F.	1200° F.	1300° F.
Ultimate, lb. per sq. in...........	81,200	49,750	39,100	31,250	23,750
Yield, lb. per sq. in......	48,000	35,750	34,250	25,000	
Elongation, per cent in 2 in	31.0	35.0	55.0	56.5	62.0
Reduction, per cent.............	68.8	81.9	89.4	93.4	96.7
Brinell hardness.............:....	161				

B

Test	Room Temperature	1000° F.	1100° F.	1200° F.	1300° F.
Ultimate, lb. per sq. in..........	84,000	39,100	35,500	21,400	13,750
Yield, lb. per sq. in.............	58,500	28,000	31,100	17,350	10,200
Elongation, per cent in 2 in......	32.0	46.0	53.0	70.0	78.0
Reduction, per cent......	63.5	78.2	83.5	92.0	96.0
Brinell hardness................	166				

Engineers design equipment on the basis of performance under nominal stress conditions, hoping to avoid rupture in service, and while rupture tests provide interesting information on an alloy's characteristics under overload, such tests will not be likely to supplant creep tests for selection of design stresses. If the rupture times are short, the lower silicon alloys offer the highest strength according to Dr. Clark's data, while if prolonged oxidation becomes a factor an intergranular surface attack may become noticeable and reduce rupture strength in the lower silicon alloys. The effect of silicon on plasticity of the ferrite at elevated temperature allows greater deformation in the higher silicon alloys before final failure.

Such results, based on laboratory tests in air atmospheres, do not necessarily follow under service conditions. Consequently large-scale adaption of silicon-containing steel alloys should proceed slowly until adequate service records in actual installations are available to support these data. For example, recent steam oxidation tests indicate that the higher silicon alloys may lose more than low-silicon ones under steam atmospheres where dissociation of steam into its components may alter the character of the protective oxide layer, permitting rapid attack of the underlying metal. Further, since the paper was written, the writer has had occasion to make comparative oxidation tests of 5 Cr high-silicon and low-silicon steel, both in air atmospheres in the laboratory and in combustion atmospheres of a boiler furnace. The results were surprisingly different, being excellent for the high-silicon material in air at 1200° and 1400° F. but about equal in the boiler tests at an average temperature approaching 1300° F. Rupture tests under varying conditions of atmosphere appear to be warranted in order to translate laboratory data to conditions approximating those encountered in service.

Previous mention has been made of hardness and of difficulty of annealing to suitable softness and in this respect our experiences coincide with Mr. E. C. Wright's.

Mr. Wilson's remarks are of interest in that commercial lots tend to give uniform and satisfactory impact values.

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(NOTE: In this index the names of authors of papers and discussions of men referred to are printed in SMALL CAPITALS, and the title of papers in *italics*.)

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